Gas-Phase Electron-Diffraction Investigation and Quantum-Chemical Calculations of the Structure of 1,5-Dimethylsemibullvalene-2,4,6,8-tetracarboxylic Dianhydride

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Dedicated to Professor *Jack D. Dunitz*. *K. H.* has known *Jack* for about 55 of his 80 years beginning when we were both post-doctoral fellows at Caltech. Those were fun times!

The bridged homotropilidines have been of interest for decades because their molecules offer the potential for homoaromaticity. Although many of these have been shown not to be homoaromatic, the energy differences of the delocalized (homoaromatic) forms and the localized (nonhomoaromatic) ones, and the barriers to the interconversion of the localized forms *via* a *Cope* rearrangement, have been found to vary greatly. The title compound is a strong candidate for homoaromaticity, and, since the structures of the possible localized and delocalized forms could differ significantly, we have carried out an electron-diffraction investigation of it augmented by quantum-mechanical calculations with different basis sets at several levels of theory. Three models were explored: one representing a localized form of C_s symmetry, one a delocalized form of C_{2v} symmetry, and one a 2 : 1 mixture of the localized/delocalized forms. Although none of the models could be ruled out, the experimental evidence slightly favors the C_s form. These results are consistent with those from the DFT B3PW91 calculations with basis sets ranging from 6-31G(d) to cc-pVTZ, which, surprisingly, predict essentially equal thermally corrected free energies for each. The results are discussed.

Introduction. – The molecular structures of the bridged homotropilidines, of which bullvalene and semibullvalene (**1**) are important examples, have been of great interest for well over three decades. One reason for this interest is that the molecules might be homoaromatic [1] as a consequence of a '*negative*' barrier to a *Cope* rearrangement [2] as illustrated below for the skeleton of semibullvalene (**1**). The homoaromatic, or delocalized, form of the molecule, **1b**, is expected to have C_{2v} symmetry, and the nonhomoaromatic, or localized, forms **1a** and **1c** should have C_s symmetry. The most obvious structural differences between the homoaromatic and localized forms lie in the nearest-neighbor distances between atoms in the six-membered ring of **1b**, and the corresponding atoms in **1a** and **1c**: in **1b** the C_2-C_3, C_3-C_4, C_6-C_7, and C_7-C_8 distances should be characteristic of C,C aromatic bonds (*ca.* 1.4 Å), while the C_2-C_8 and C_4-C_6 distances are expected to be elongated (*ca.* 2 Å), but in **1a** (**1c**) their values as double, single, and nonbonds are anticipated [3].

There is abundant experimental and theoretical evidence that the ground state of semibullvalene itself is not homoaromatic (for a summary of current information about

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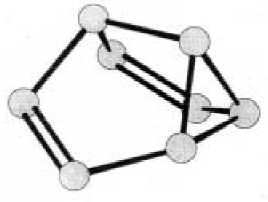
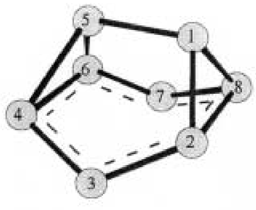
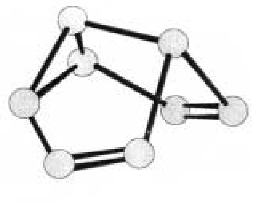


1a



1b



1c

semibullvalenes and homoaromaticity, see [4]). On the experimental side, *Wang* and *Bauer* [5] concluded that their gas-phase electron-diffraction data favored a molecule of C_s symmetry, *i.e.*, one corresponding to a localized ground state, a result consistent with NMR data [6][7]. Results for a number of substituted semibullvalenes are similar [4], but are found to differ substantially in the barrier to the *Cope* rearrangement. For example, the barrier (ΔG^{+}) in semibullvalene is 6.2 kcal/mol at 298 K [7], but several derivatives with electron-withdrawing substituents at some or all of the 2, 4, 6, and 8 positions have significantly lower barriers [8], although as yet no example of a homoaromatic ground state (where the barrier is effectively negative) has been characterized. The problem is further complicated by the observation that the homoaromatic form of some of these molecules is favored over the localized one in a highly dipolar solvent [9], whereas the reverse is found in less-polar solvents, which suggests that, for these compounds, the more-stable form in the gas should be the localized one.

A promising candidate for demonstration of a homoaromatic ground state is the molecule 1,5-dimethylsemibullvalene-2,4,6,8-tetracarboxylic dianhydride [10][11] (hereafter SBDA) diagrammed in *Fig. 1*. In principle, the two dicarboxylic anhydride moities induce significant strain that destabilizes the localized form of the semibullvalene skeleton relative to the homoaromatic one. In the crystal, however, at 15 K, [12] SBDA was found to exist as a single tautomer of the localized structure, and, in the temperature range of 293–240 K, the system is dynamically disordered, indicating an equilibrium between tautomers [10][12]. Comparison of experimental results for SBDA (all in condensed phases) with theoretical predictions led to a fascinating dichotomy [4]: HF/6-31G(d) and HF/6-311G(d,p) optimizations of the structure gave localized ground states with a delocalized transition state ($\Delta H^{+} = 7.49$ kcal/mol), but inclusion of electron correlation at the DFT and MP2 levels of theory (B3LYP/6-31G(d) and MP2/6-31G(d)) led to a single minimum in the rearrangement coordinate and, thus, to a structure of C_{2v} symmetry corresponding to the delocalized form. Interestingly, single-point B3LYP/6-31G(d) and MP2/6-31G(d) calculations at the HF stationary points led to *lower* energies for the symmetric than for the localized forms by 2.08 and 4.4 kcal/mol, respectively. These facts – that the correlated optimizations as well as the single-point-correlated calculations at the stationary points are only consistent with a homoaromatic ground state – led one of us to speculate that matrix effects profoundly influence the relative stabilities of the two forms, and that the homoaromatic one is perhaps the ground state in the gas phase [4]. Recently, we have gained some support for this contention from UV/VIS studies [13], similar to those of *Seefelder* and *Quast* [9a], that indicate that the delocalized form is stabilized relative to the localized form in solvents of *low* polarity. In an attempt to shed further light on this question, we have carried out an electron-diffraction investigation of SBDA as well as a number of *ab initio* and DFT calculations with a variety of basis sets. This article describes our results.

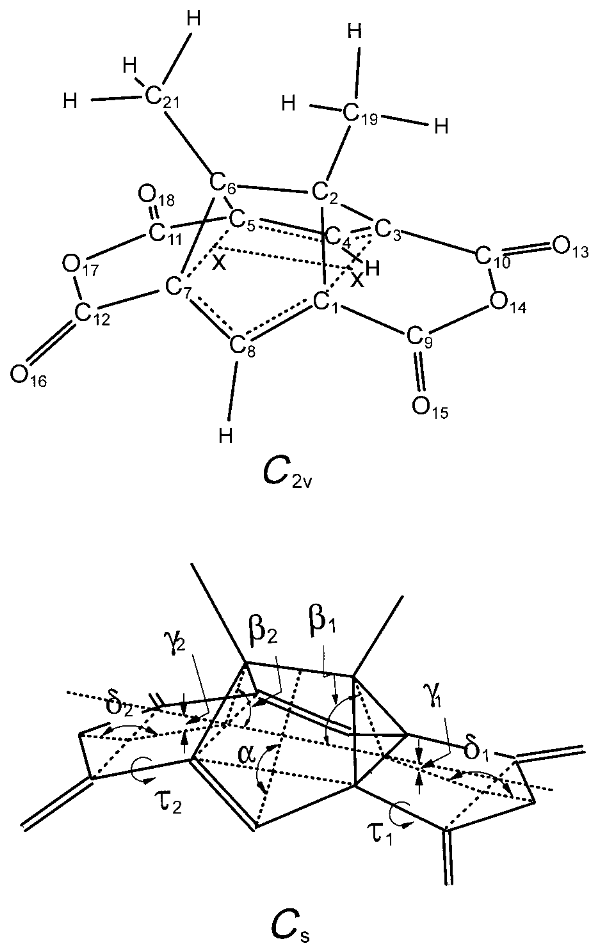


Fig. 1. *Diagrams of the two forms of 1,5-dimethylsemibullvalene-2,4,6,8-tetracarboxylic dianhydride* (SBDA). The atom numbering is shown on the C_{2v} form and the special angle parameters on the C_s form.

Theoretical Calculations. – Our quantum-mechanical calculations were carried out with the Gaussian98 and Gaussian98W packages [14] at the HF, B3LYP, and B3PW91 levels of theory with the bases 6-31G(d), 6-311++G(d,p), and cc-pVTZ. For convenience in doing the calculations with larger bases, some of the calculations with the 6-31G(d) basis duplicated the work cited in the previous paragraph. The optimizations were carried out in pairs, beginning with a model of either C_{2v} or C_s symmetry, and carried to convergence. In each case, a vibrational frequency test was performed in order to ascertain whether the optimized structure corresponded to a ground or to a transition state. *Tables 1* and *2* contain a summary of the results from most of the calculations. As *Table 1* shows, the calculations predict the localized (C_s) form to be the ground state at the HF level of theory regardless of basis-set size, and the delocalized (C_{2v}) form to be a transition state. On the other hand, the delocalized form was found to be the ground state from DFT theory at the B3LYP level, and evidence for a transition state did not appear; instead, calculations started from a structure similar to one of the optimized, localized forms converged to a delocalized one. Finally, to further complicate the picture, DFT theory at the B3PW91 level predicts that the two forms are equally stable regardless of basis set, and that neither is a transition state. It is evident that theory at these moderately high levels does not allow a reliable choice of the ground state form to be made.

Table 1. *Total Electronic Energies and* Gibbs *Free Energies of 1,5-Dimethylsemibullvalene-2,4,6,8-tetracarboxylic Dianhydride* (SBDA) *from Several Levels of Theory and Basis Sets*

Basis	Sym.	HF[a])	B3LYP[b])	B3PW91[c])	
		$E_h = -983.0 +$	$E_h = -989.0 +$	$E_h = -989.0 +$	$G^\circ = -989.0 +$
6-31G(d)	C_s	– 0.9616794	–	– 0.2381067	– 0.1336997
	C_{2v}	– 0.9485448*	– 0.6039265	– 0.2379835	– 0.1335695
	Δ[d])	– 8.6 kcal/mol		– 0.081	– 0.082
6-311++G(d,p)	C_s	– 1.2014535	–	– 0.4936164	– 0.3911044
	C_{2v}	– 1.1875930*	– 0.8751453	– 0.4934727	– 0.3913224
	Δ[d])	– 9.1 kcal/mol		– 0.094	0.137
cc-pVTZ	C_s	– 1.2995914	–	– 0.5732208	– 0.4704108
	C_{2v}	– 1.2861166*	– 0.9549034	– 0.5732280	– 0.4704180
	Δ[d])	– 8.9 kcal/mol		0.005	0.005

[a]) Asterisks denote transition state. [b]) Optimizations started at C_s symmetry converged to C_{2v}. [c]) Stable ground states found for each symmetry. [d]) Differences are values for C_s minus C_{2v}.

In addition to the structural evidence offered by the quantum-mechanical calculations, the calculations also yielded quadratic vibrational force fields that permitted normal coordinate analyses of the structures. These analyses were carried out with the program ASYM40 [15]. Among other things, they provided estimates of amplitudes of vibration that were experimentally inaccessible, and correction terms allowing interconversion of different types of interatomic distances²).

Experimental. – The sample of SBDA was synthesized [10] at the University of Idaho and sent to Oregon State University, where it was used without further purification in the electron-diffraction (GED) experiments.

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²) These distances are symbolized as r_α, the distance between average nuclear *positions*; r_g, the thermal average *distance*; and r_a, the parameter figuring in the scattered intensity. The relations between these quantities are $r_g = r_a + l^2/r = r_\alpha + \Delta r = r_\alpha + \langle \Delta z \rangle + \mathrm{K}$, where l^2 is a mean-square amplitude of vibration, $\mathrm{K} = (\langle \Delta x^2 \rangle + \langle y^2 \rangle)/2r_e$, $\Delta z = r - r_e$, and Δy and Δz displacements perpendicular to r. More details about these quantities may be found in papers from ours and other laboratories.

Table 2. *Some Theoretical Interatomic Distances* (r_e) *for 1,5-Dimethylsemibullvalene-2,4,6,8-tetracarboxlic Dianhydride* (SBDA)[a])

	HF			B3LYP			B3PW91					
Basis [b]):	A	B	C	A	B	C	A		B		C	
Sym.:	C_s	C_s	C_s	C_{2v}	C_{2v}	C_{2v}	C_{2v}	C_s	C_{2v}	C_s	C_{2v}	C_s
Semibullvalene moitey												
⟨CH⟩	1.080	1.081	1.079	1.092	1.087	1.087	1.092	1.092	1.090	1.090	1.088	1.088
C_2C_6	1.548	1.547	1.545	1.565	1.556	1.562	1.557	1.551	1.556	1.549	1.553	1.547
C_1C_7	2.272	2.272	2.268	2.266	2.256	2.258	2.259	2.274	2.256	2.271	2.252	2.267
C_4C_8	3.117	3.112	3.104	3.274	3.217	3.259	3.220	3.135	3.218	3.128	3.201	3.118
C_1C_5	2.958	2.958	2.952	3.080	3.043	3.072	3.043	2.983	3.043	2.981	3.034	2.974
C_1C_2	1.495	1.496	1.492	1.512	1.507	1.508	1.507	1.506	1.507	1.505	1.504	1.502
C_6C_7	1.520	1.520	1.518					1.520		1.519		1.516
C_1C_3	1.602	1.601	1.598	2.086	2.043	2.082	2.039	1.709	2.043	1.708	2.033	1.708
C_5C_7	2.239	2.240	2.234					2.179		2.181		2.170
C_1C_8	1.467	1.467	1.464	1.392	1.387	1.385	1.390	1.439	1.387	1.438	1.384	1.434
C_7C_8	1.330	1.329	1.325					1.359		1.355		1.352
C_2C_{19}	1.511	1.510	1.507	1.522	1.513	1.516	1.615	1.507	2.612	1.505	1.510	1.502
C_6C_{21}	1.524	1.523	1.520					1.509		1.516		1.513
C_1C_4	2.673	2.671	2.665	2.960	2.915	2.950	2.915	2.726	2.915	2.722	2.902	2.727
C_4C_7	2.958	2.956	2.948					2.946		2.943		2.932
C_2C_4	2.424	2.424	2.418	2.409	2.402	2.400	2.405	2.422	2.402	2.420	2.396	2.413
C_4C_6	2.368	2.368	2.362					2.388		2.386		2.380
C_1C_6	2.372	2.373	2.368	2.404	2.404	2.409	2.406	2.391	2.404	2.389	2.400	2.385
C_2C_7	2.416	2.415	2.411					2.419		2.416		2.412
Anhydride moieties												
C_1C_9	1.488	1.487	1.485	1.472	1.472	1.471	1.474	1.439	1.472	1.480	1.470	1.478
C_7C_{12}	1.483	1.484	1.482					1.476		1.475		1.473
C_9O_{15}	1.172	1.167	1.167	1.192	1.192	1.192	1.198	1.196	1.192	1.189	1.191	1.189
$C_{12}O_{16}$	1.174	1.168	1.168					1.198		1.191		1.190
C_9O_{14}	1.362	1.359	1.357	1.390	1.390	1.395	1.392	1.389	1.390	1.387	1.388	1.385
$C_{12}O_{17}$	1.370	1.369	1.366					1.396		1.396		1.393

[a]) See *Fig. 1* for atom numbering. [b]) Basis sets: A = 6-31G(d), B = 6-311 + + G(d,p), C = cc-pVTZ.

A series of photographs were taken at both the long (LC) and middle camera (MC) distance, 754 and 301 mm resp., using an electrically heated high-temperature oven [16]. Since the vapor pressure suitable for a diffraction experiment was unknown, the oven was slowly heated, and the needle valve was opened periodically until sufficient electron scattering was observed on the alignment screen. Nozzle-tip temp. of 222 to 260° were necessary to produce adequate amounts of sample vapor for the diffraction experiments. Other experimental conditions included: beam currents of 0.72–0.83 μA; exposure times of 1.5 to 4.0 min; an r^3 sector; 8 in × 10 in Kodak electron-image film developed in *D-19* developer diluted 1 to 1; and a 60-kV electron accelerating potential. The electron wavelength was determined in separate experiments with use of CO_2 (r_a(C–O) = 1.1646 Å, r_a(O–O) = 2.3244 Å) as the calibration standard.

Four films from the LC distance and two from the MC were selected for analysis. Procedures similar to those described in [17] were used to obtain the total scattered intensities (s^4I_T) and to subtract backgrounds. Each of the experimental intensity curves presented in *Fig. 2* is the average of three microphotometric traces of a film executed to enhance ring intensities and reduce background noise. These curves with backgrounds removed are shown below. Ranges of the data were $2.0 \leq s/\text{Å}^{-1} \leq 16.25$ and $8.0 \leq s/\text{Å}^{-1} \leq 39.25$ at intervals $\Delta s = 0.25$ Å^{-1}. The data for the background-subtracted curves may be obtained from the authors.

The experimental radial-distribution curve is shown in *Fig. 3*. It was obtained by leveling the background-subtracted intensity curves by multiplication with the factor $(Z_C/A_C)^2 \exp(-0.002s^2)$ and forming a composite of

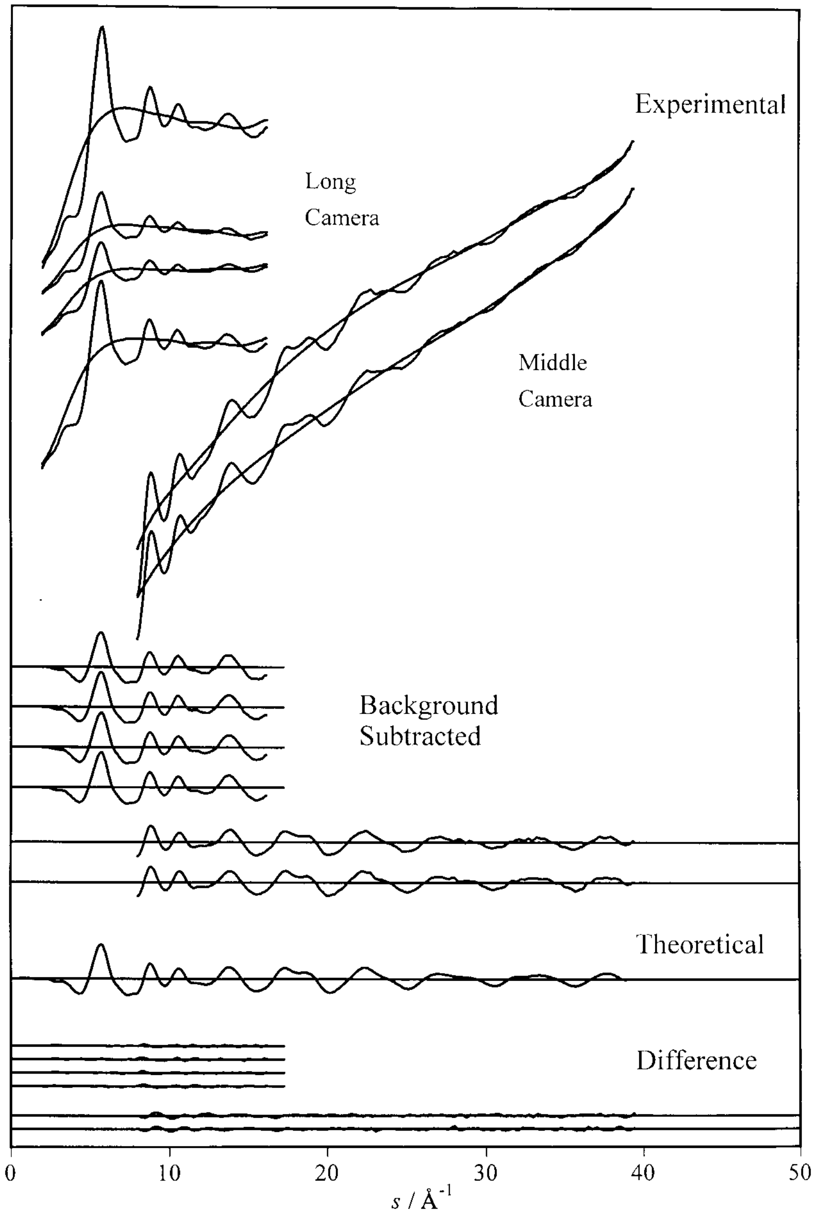

Fig. 2. *Scattered intensity distribution from electron diffration of 1,5-dimethylsemibullvalene-2,4,6,8-tetracarboxylic dianhydride* (SBDA). Curves of the data from each film, amplified five times, are shown superimposed on their backgrounds. Each curve is the average of three microphotometric traces. The background-subtracted curves represent the molecular scattering on which the refinements were based. The difference curves are experimental minus theoretical intensities for the three models indicated.

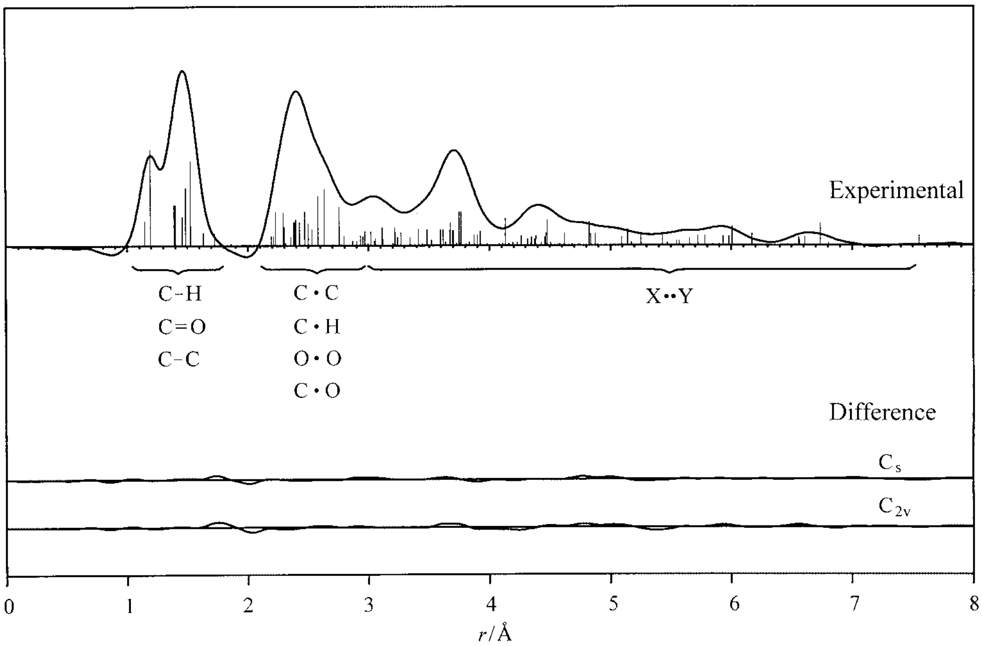

Fig. 3. *Radial-distribution curves for 1,5-dimethylsemibullvalene-2,4,6,8-tetracarboxylic dianhydride* (SBDA). The positions of the vertical bars represent the interatomic distances in the C_s model. The lengths of the bars are proportional to weights of the terms. The regions in brackets indicate the locations of the bond distances, distances across a bond angle, and the remaining longer distances.

them before *Fourier* transformation. Intensity data in the inaccessible region $s \leq 2.0$ Å^{-1} were taken from the final theoretical curve[3]).

Structure Analysis. – *Formulation of the Models.* Electron diffraction operates at its best on molecules with high symmetry where the geometry can be described by a relatively small number of parameters, and where many of the interatomic distances are well-separated from each other. This is not the case for SBDA, and, therefore, the results of the structure analysis will depend on a number of assumptions. Further, the experimental diffraction patterns for SBDA expected from molecules of C_s symmetry with localized bonds and homoaromatic ones of C_{2v} symmetry should be very similar. The reason is that, with the exception of the nearest-neighbor distances in the six-membered ring, most of the other interatomic distances in models of each symmetry are not expected to be much different.

To specify the structure of an SBDA homoaromatic molecule assumed to have overall C_{2v} symmetry, with C_{3v} symmetry for the $C-CH_3$ groups requires 18 parameters, but a localized one of C_s symmetry requires 32. In each case, these are far too many to be measured reliably, especially when the effect of a great many more vibrational amplitude parameters must also be considered. What did seem possible in the face of

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[3]) The data were from the C_s model, but those from the C_{2v} model are virtually identical in this region.

this daunting problem was to ascertain, with the help of some constraining assumptions suggested by the theoretical calculations, which, if either, of the two symmetries led to the best fit to the diffraction data. To make comparisons simpler, we formulated the structural parameters for the C_s version of the molecule in terms of averages and differences, which, when the differences were set to zero, automatically generated the C_{2v} version. The atom numbering for molecules of each symmetry is shown in the upper diagram of *Fig. 1*. The following examples illustrate the meanings of the symbols for bond-distance and bond-angle parameters in molecules of C_s symmetry. $\langle r(C_1C_9;C_7C_{12})\rangle = [r(C_1{-}C_9) + r(C_7{-}C_{12})]/2$ with $\Delta r(C_1C_9;C_7C_{12}) = r(C_1{-}C_9) - r(C_7{-}C_{12})$; $\langle\angle\ (C_3C_1C_9;C_5C_7C_{12})\rangle = [\angle\ (C_3{-}C_1{-}C_9) + \angle\ (C_5{-}C_7{-}C_{12})]/2$ with $\Delta\ \angle\ (C_3C_1C_9;C_5C_7C_{12}) = \angle\ (C_3{-}C_1{-}C_9) - (C_5{-}C_7{-}C_{12})$. The remaining parameters, which are seen in the diagram of C_s symmetry, are a distance $r(XX)$ between the midpoints of the lines $r(C_1C_3)$ and $r(C_5C_7)$, and some interplanar and torsion angles indicated by Greek letters. Thus, β_1 is the angle between $r(XX)$ and the plane $C_1C_2C_3$, γ_1 is the angle between the projection of $r(XX)$ and the plane $C_1C_3C_{10}C_9$, δ_1 is the angle between the planes $C_1C_3C_{10}C_9$ and $C_9C_{14}C_{10}$, and τ_1 is the torsion angle $C_3C_1C_9O_{15}$. The average angle parameters were formulated as illustrated for the distances, and in all cases the difference parameters are the first named distance/angle minus the second[4]. The complete set of geometrical parameters is seen in the first column of *Table 3*. These parameters contain two simplifying assumptions: all C−H bond lengths were assumed equal, as were all C−C−H bond angles. The models were defined by parameters in r_α space where the restrictions of symmetry apply exactly, but which required use of distance corrections[2]) in the fitting procedure. We used the Cartesian force fields from the B3PW91/cc-pVTZ optimizations (which yielded stable minima for molecules of both C_s and C_{2v} symmetry) in the ASYM40 program to calculate these quantities as well as amplitudes of vibration. All interatomic distances were included in each model. One other model was tested. It was inspired by the ambiguous results predicted from our quantum-mechanical calculations for the ground state of the molecule – whether it is the localized C_s or delocalized C_{2v} form. The model was intended to represent roughly a dynamic system of the two conformers assumed to be of equal free energies; it consisted of C_s/C_{2v} ratio of 2:1 of the two forms, which is consistent with their degeneracies. The parameters of the C_{2v} form were tied to the corresponding average ones of the C_s form (for example, $r(C_1C_9;C_7C_{12})$ in C_{2v} was tied to $\langle r(C_1C_9;C_7C_{12})\rangle$ in C_s) by the experimental differences taken from the results of the refinements of the C_s and C_{2v} models. The mixture model was, thus, specified by the values of the C_s component.

To complete the description of the three models, the values of vibrational amplitude parameters are needed. There is one such parameter for each interatomic distance in the molecule, a number much too large (*ca.* 75 exclusive of terms involving H-atoms) for independent refinement of each. Some of the amplitudes could be formed into groups within which the differences between group members was kept unchanged during refinement, but the values of most amplitudes were taken from the calculations mentioned above.

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[4]) All numbering is from *Fig. 1*. For convenience in formulating the computer program for description of the models, it differs from the numbering in the title compound.

Table 3. *Parameter Values* (r/Å, $\angle$/deg) *for Models of 1,5-Dimethylsemibullvalene-2,4,6,8-tetracarboxylic Dianhydride* (SBDA)[a]

	Experiment			Theory[b]	
Model:	C_s	C_{2v}	$C_s + C_{2v}$[c]	C_s	C_{2v}
Parameter[d]	r_α; $\angle_e$	r_α; $\angle_e$	r_α; $\angle_e$	r_α; $\angle_e$	r_α; $\angle_e$
$\langle r(C-H)\rangle$	[1.088]	[1.087]	[1.088]	1.088	1.088
$\langle r(C_1C_9;C_7C_{12})\rangle$	1.511 (10)	1.526 (8)	1.527 (11)	1.475	1.470
$\Delta r(C_1C_9;C_7C_{12})$	– 0.007 (21)	–	0.008 (32)	0.005	–
$\langle r(C_1C_8;C_7C_8)\rangle$	1.422 (13)	1.371 (10)	1.413 (14)	1.393	1.384
$\Delta r(C_1C_8;C_7C_8)$	0.069 (24)	–	0.089 (32)	0.081	–
$\langle r(C_1C_2;C_6C_7)\rangle$	1.487 (14)	1.479 (10)	1.474 (11)	1.509	1.504
$\Delta r(C_1C_2;C_6C_7)$	– 0.034 (29)	–	0.007 (35)	– 0.014	–
$\langle r(C_5C_7;C_1C_3)\rangle$	1.989 (19)	2.266 (44)	1.974 (55)	1.939	2.033
$\Delta r(C_5C_7;C_1C_3)$	0.471 (30)	–	0.486 (35)	0.462	–
$\langle r(C_2C_{19};C_6C_{21})\rangle$	1.533 (15)	1.531 (26)	1.527 (27)	1.508	1.510
$\Delta r(C_2C_{19};C_6C_{21})$	– 0.009 (29)	–	– 0.013 (36)	– 0.011	–
$\langle r(C_9O_{15};C_{12}O_{16})\rangle$	1.168 (2)	1.171 (2)	1.168 (2)	1.189	1.191
$\Delta r(C_9O_{15};C_{12}O_{16})$	[– 0.002]	–	[– 0.002]	– 0.002	–
$\langle r(C_9O_{14};C_{12}O_{17})\rangle$	1.383 (9)	1.417 (8)	1.394 (9)	1.389	1.388
$\Delta r(C_9O_{14};C_{12}O_{17})$	0.008 (23)	–	0.004 (33)	– 0.007	–
$R(XX)$	2.291 (15)	2.193 (13)	2.324 (24)	2.256	2.252
$\langle \angle(CCH)\rangle$	[110.9]	[110.9]	[110.9]	110.9	110.9
$\langle \angle(C_6C_2O_{19};C_2C_6C_{21})\rangle$	138.6 (12)	1.386 (17)	141.3 (14)	119.6	119.2
$\Delta\angle(C_6C_2O_{19};C_2C_6C_{21})$	[0.4]	–	[0.4]	3.861	–
$\langle \angle(C_1C_9O_{15};C_7C_{12}C_{16})\rangle$	125.6 (10)	120.9 (14)	126.8 (13)	127.2	126.3
$\Delta\angle(C_1C_9O_{15};C_7C_{12}C_{16})$	10.1 (28)	–	11.1 (34)	0.724	–
$\langle \angle(C_3C_1C_9;C_5C_7C_{12})\rangle$	97.3 (4)	91.6 (8)	98.2 (12)	98.2	96.3
$\Delta\angle(C_3C_1O_9;C_5C_7C_{12})$	7.4 (7)	–	7.8 (11)	6.9	–
α	139.3 (33)	121.6(50)	132.5 (31)	136.6	136.6
$\langle\beta\rangle$	73.3 (10)	73.8 (88)	74.0 (10)	107.9	108.4
$\Delta\beta$	0.8 (21)	–	– 5.9 (45)	– 4.3	–
$\langle\gamma\rangle$	16.9 (15)	14.8 (14)	18.6 (16)	122.7	125.6
$\Delta\gamma$	– 9.5 (43)	–	– 10.1 (48)	– 8.2	–
$\langle\delta\rangle$	166.7 (32)	150.0 (56)	159.1 (32)	164.4	160.1
$\Delta\delta$	[4.5]	–	[4.5]	4.5	–
$\langle\tau\rangle$	170.0 (52)	172.7 (61)	154.5 (60)	171.1	169.1
$\Delta\tau$	[0.9]	–	[0.9]	0.9	–
R	0.091	0.106	0.103		

[a] Quantities in parentheses are estimated 2σ uncertainties. Those in brackets were assumed. [b] B3PW91/cc-pVTZ. [c] Model consisting of 67% C_s, 33% C_{2v}. [d] Parameter values are those of the C_s component.

Structure Refinements. Refinement of the models was achieved in the usual way by the method of least-squares in which a theoretical intensity function corresponding to a model was fitted simultaneously to the six experimental background-subtracted intensity curves [18]. A total of 199 interatomic distances each were generated by the C_s and C_{2v} models, and 398 by the mixture model (some of the distances were duplicates in the C_{2v} forms). For the C_{2v} model, we were able to refine 16 of the 18 geometric parameters and 10 of the group-amplitude parameters simultaneously in the final cycle of the least-squares fitting. The situation was different for the more-complicated C_s model, but by making use of 'predicates' [19] estimated from theory and assigned to all difference parameters except $\Delta r(C_9O_{15};C_{12}O_{16})$, $\Delta\angle(C_6C_2O_{19};C_2C_6C_{21})$, $\Delta\delta$, and $\Delta\tau$, we were able to obtain values for 26 variables and 10 vibrational amplitudes. The results for the C_s and C_{2v} models from these refinements are found in *Table 3*. *Table 4* contains a selection of the more important interatomic distances from these two models; the full list of distances for all models is available from the corresponding author. Results for the mixture model are not included because they are, as expected, essentially an average of those for the C_s and C_{2v} models.

Results and Discussion. – It was hoped that a study of the fits of the localized and delocalized models to the electron-diffraction data would reveal with near certainty which of these forms is most likely the predominant one for SBDA in the gas phase. Unfortunately, this is not the case; although there are differences in the quality of fit provided by the three models, we do not feel the differences are large enough to *rule out*

Table 4. *Experimental* (r_α, r_g, r_a) *and Theoretical* (r_e) *Values for Selected Distances* (r/Å) *and Vibrational Amplitudes* (*l/Å*) *for Models of 1,5-Dimethylsemibullvalene-2,4,6,8-tetracarboxylic Dianhydride* (SBDA)[a])

	Model of C_s symmetry[b])						Model of C_{2v} symmetry[c])					
	r_α	r_g	r_a	l_{exp}	r_e	l_{theo}	r_α	r_g	r_a	l_{exp}	r_e	l_{theo}
Semibullvalene moiety												
C–H	[1.088]	1.152 (1)	1.146	[0.081]	1.088	0.081	[1.088]	1.143	1.137	[0.078]	1.088	0.078
C_2C_6	1.631	1.635 (20)	1.633	0.051 (4)[d])	1.547	0.060	1.662	1.665 (18)	1.664	0.046 (6)	1.553	0.057
C_1C_7	2.295	2.303 (29)	2.302	0.035 (12)[g])	2.267	0.062	2.193	2.206 (13)	2.206	0.037 (10)	2.252	0.057
C_4C_8	3.114	3.120 (130)	3.118	0.093 (21)[e])	3.118	0.114	3.131	3.137 (105)	3.130	0.150 (34)	3.201	0.116
C_1C_5	3.014	3.020 (26)	3.018	0.069 (21)[e])	2.974	0.090	3.154	3.160 (35)	3.155	0.122 (34)	3.034	0.088
C_1C_2	1.452	1.460 (22)	1.459	0.050 (4)[d])	1.502	0.059	1.479	1.488 (10)	1.487	0.044 (6)	1.504	0.056
C_6C_7	1.487	1.493 (23)	1.491	0.050 (4)[d])	1.516	0.059						
C_1C_3	1.731	1.737 (44)	1.725	0.146 (7)[d])	1.708	0.155	2.266	2.272 (44)	2.259	0.172 (9)	2.033	0.183
C_5C_7	2.207	2.212 (38)	2.210	0.071 (12)[g])	2.107	0.099						
C_1C_8	1.477	1.485 (32)	1.483	0.048 (4)[d])	1.434	0.057	1.371	1.380 (10)	1.379	0.043 (6)	1.384	0.055
C_7C_8	1.385	1.393 (35)	1.392	0.039 (4)[d])	1.352	0.048						
C_2C_{19}	1.509	1.524 (34)	1.523	0.047 (4)[d])	1.502	0.056	1.531	1.543 (26)	1.541	0.043 (6)	1.510	0.054
C_6C_{21}	1.521	1.534 (35)	1.533	0.048 (4)[d])	1.513	0.057						
C_1C_4	2.752	2.758 (46)	2.755	0.102 (13)[f])	2.717	0.116	2.996	3.002 (47)	2.999	0.096 (14)	2.902	0.124
C_4C_7	2.965	2.971 (47)	2.968	0.087 (13)[f])	2.932	0.101						
C_2C_4	2.460	2.467 (27)	2.466	0.038 (12)[g])	2.413	0.066	2.396	2.402 (25)	2.401	0.042 (10)	2.396	0.062
C_4C_6	2.385	2.391 (48)	2.391	0.036 (12)[g])	2.380	0.064						
C_1C_6	2.374	2.380 (26)	2.379	0.039 (12)[g])	2.385	0.067	2.415	2.421 (9)	2.420	0.045 (10)	2.400	0.065
C_2C_7	2.469	2.474 (31)	2.473	0.041 (12)[g])	2.412	0.068						
Anhydride moieties												
C_1C_9	1.524	1.535 (19)	1.534	0.047 (4)[d])	1.478	0.056	1.527	1.538 (8)	1.536	0.042 (6)	1.470	0.053
C_7C_{12}	1.513	1.523 (20)	1.521	0.047 (4)[d])	1.473	0.056						
C_9O_{15}	1.167	1.194 (2)	1.192	0.043 (3)[h])	1.189	0.039	1.171	1.196 (2)	1.194	0.044 (3)	1.191	0.038
$C_{12}O_{16}$	1.169	1.196 (2)	1.194	0.043 (3)[h])	1.190	0.039						
C_9O_{14}	1.390	1.403 (26)	1.402	0.048 (4)[d])	1.385	0.057	1.417	1.430 (8)	1.429	0.044 (6)	1.388	0.055
$C_{12}O_{17}$	1.377	1.392 (21)	1.391	0.050 (4)[d])	1.393	0.059						

[a]) Quantities in square brackets are calculated from B3LYP/6-311++G(d,p) force field and were not refined. Quantities in parentheses are estimated 2 σ uncertainties. See *Fig. 1* for atom numbering. [b]) Localized bonding. [c]) Delocalized bonding. [d]), [e]), [f]), [g]), [h]) Amplitudes refined in groups.

any of them. However, it is possible to judge which is *more likely* to be the major component, and that appears to be the form of C_s symmetry with localized bonds. The quality of the fit provided by this model, seen visually in the difference curves of *Figs. 2* and *3*, and in the smaller value for the factor R in *Table 4*, is better than that for the delocalized model of C_{2v} symmetry.

Since the qualities of fit to the diffraction data provided by the models of localized and delocalized bonding do not afford us a *definitive* choice from the experimental side, and, therefore, offer no clue as to the reliability of any of the theoretical predictions, it is uncertain about how to interpret this group of experimental and theoretical results. However, if the assumption is made that the results from B3PW91 theory are most likely to reflect reality, the prediction of equal energies for the two forms suggests that the gaseous material might well be a mixture of them. Our third model consisting of the 2:1 mixture of the localized/delocalized forms provides a fit to the diffraction data intermediate between those from the localized and delocalized models alone ($R(\text{mix}) = 0.103$, $R(C_s) = 0.099$, $R(C_{2v}) = 0.106$). The mixture model of only two components implies a significant barrier to component interconversion. However, the actual circumstance could be more complicated. If the barrier is low, say ≤ 1 kcal/mol, substantial numbers of molecules with intermediate structures will also exist. The model for such a system would be a dynamic one that incorporated a group of 'pseudoconformers' distributed along the conversion coordinate in amounts determined by a *Boltzmann* weighting, $N(q)/N_T = \exp(-V(q)/RT)$, dependent on the *Cope* rearrangement potential $V(q)$. A detailed GED exploration of such a dynamic model is impractical because we do not know $V(q)$ in the many-parameter space defining the geometry of SBDA. There is weak evidence, however, that dynamic behavior of the SBDA system with substantial fractions of pseudoconformers distributed along the *Cope* rearrangement path is less likely than the two-conformer system. If one defines the range of the *Cope* rearrangement coordinate to be $0.0 \leq q \leq 1.0$, and assumes that the structures of the molecules at q equal to ± 1.0 (the optimized C_s form) and 0.0 (the optimized C_{2v} form) *differ* by the amounts obtained from the B3PW91/cc-pVTZ optimizations of each, then it is possible to calculate the energy of a pseudoconformer at any q by the further assumption that each parameter p changes from the C_{2v} value by $q[p(C_s) - p(C_{2v})]$. We have carried out single-point energy calculations at the level cited for several values of q. The relative values, $\Delta E/(\text{kcal/mol})$, are 0.0, 2.2, 2.3, 2.2, and 0.0 at $q = 0.0$, 0.25, 0.50, 0.75, and 1.0. These energies suggest a plateau in $V(q)$, which seems not to be high, but is sufficient to reduce the number of molecules in the region $0.25 \leq q \leq 0.75$ to *ca.* 10% of those found for the optimized C_s and C_{2v} forms. In sum, we find no evidence that the mixture model is better than the model of C_s symmetry with localized bonding.

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