The Cope Rearrangement of 1,5-Dimethylsemibullvalene-2,6- and 3,7-dicarbonitriles in the Solid State

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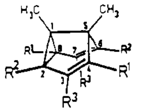
The degenerate Cope rearrangement in suitably substituted semibullvalenes is of considerable interest because some substitution patterns may result in systems having bishomoaromatic ground states.[1] Available X-ray crystallographic structures for some possible candidates, **1a**,[2] **1b**,[3a] **1c**,[3a] **1d**,[4] appear to be consistent with a single, nonexchanging valence tautomer having 2–8 and 4–6 internuclear distances which are longer and shorter, respectively (see Table I for the values for **1a** and **1b**), than the normal distances found in unsymmetrically substituted derivatives.[2b] Yannoni and his co-workers,[5] however, have shown by low-temperature CP-MAS ^{13}C NMR spectroscopy that semibullvalene itself can form a solid phase in which the Cope rearrangement is fast on the NMR time scale but in which the degeneracy is slightly perturbed (i.e., $K_{eq} \neq 1$ for the rearrangement). No X-ray structure is available for this system. We now present similar studies of the molecules **1a** and **b**, which show that the observation of anomalous 2–8 and 4–6 internuclear distances in their X-ray structures is a consequence of dynamic disorder associated with a rapid, nondegenerate Cope rearrangement.



1a: $R^1 = R^3 = H$, $R^2 = CN$
1b: $R^1 = R^2 = H$, $R^3 = CN$
1c: $R^1 = R^2 = H$, $R^3 = CO_2CH_3$
1d: $R^1 = R^2 = CO_2CH_3$, $R^3 = H$

In addition to the crystalline modification (α-form) for which the X-ray structure of **1a** has been reported,[2] we have now obtained a second form (β) which belongs to the same space group with two racemic pairs of molecules in the unit cell but having significantly different cell dimensions.[6] In the β-form *the molecules have apparent C_2 symmetry, i.e., the 2–8 and 4–6 distances are apparently equal* (Figure 1 and Table I)! Distances differing appreciably from those expected for a classical structure have also been found for the 3,7-dicarbonitrile **1b** at both 298 and 173 K, and it is significant that they exhibit an appreciable temperature dependence.[3a]

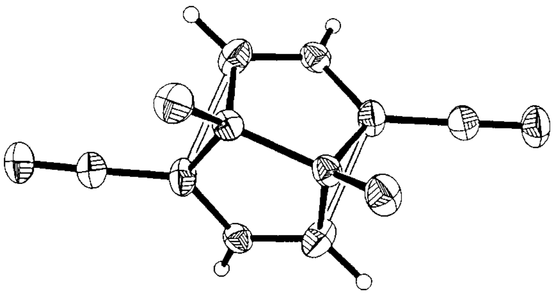


Figure 1. ORTEP view of **1a** in the β-form.

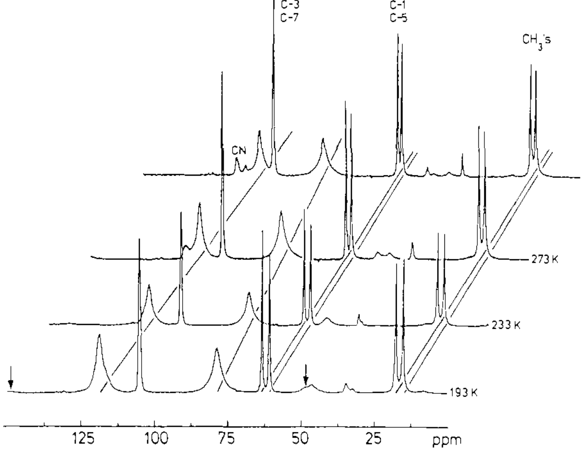


Figure 2. 74.9 MHz CP-MAS ^{13}C spectra of **1b**. The arrows indicate the limiting chemical shifts for C(4)/C(6) and C(2)/C(8) from low temperature solution spectra.

We have examined the 74.9 MHz CP-MAS ^{13}C spectra[7] of these three crystalline samples. The spectra are readily assigned on the basis of chemical shifts, dipolar dephasing experiments,[8] and the observation that the nitrile carbons and, at 25 MHz, those α to the nitrile groups exhibit dipolar coupling to the neighboring ^{14}N nucleus.[9] The variable temperature spectra of **1b** are reproduced in Figure 2. The dramatic temperature dependence of the chemical shifts of the C(2)/(8) and C(4)/(6) resonances is not associated with any observable change in line shapes and must therefore be associated with a nondegenerate Cope rearrangement which is fast on the ^{13}C NMR time scale over the temperature range of the observations. Similar results are obtained with both the α- and β-forms of **1a** (Figures 3 and 4, respectively). In the case of the β-form, the rearrangement is fortuitously degenerate at room temperature but is nondegenerate at both higher and lower temperatures. The small splittings observed for the pairs of resonances of C(3)/(7), C(1)/C(5), and the nitrile carbons at room temperature are not associated with the Cope equilibrium and must be the result of nonequivalent environments in the crystal.

Since the Cope rearrangements in these systems are fast on the ^{13}C NMR time scale, equilibrium constants for the valence tau-

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(6) Crystal data for the β-form of **1a**: $C_{12}H_{10}N_2$; $M_r = 182.22$, monoclinic, space group $P2_1/a$ (no. 14); $a = 1235.7$ (4) pm, $b = 716.1$ (3) pm, $c = 1128.0$ (3) pm, $\beta = 91.95$ (2)°; $V = 997.5$ (6) $\times 10^{-6}$ pm^3, $Z = 4$; $D_c = 1.213$ g cm^{-3}; λ(Mo Kα) = 71.07 pm, μ(Mo Kα) = 0.71 cm^{-1}, absorption correction: Ψ-scan. The intensities of 2061 reflections were measured on a Nicolet R3m/V diffractometer at room temperature ($3.5 \leq 2\theta \leq 50.0$). The structure was solved by direct methods and refined by full-matrix least squares using 1322 unique observed reflections ($F \geq 3.0\sigma(F)$). The reflection to parameter ratio was 9:1. The final residuals were $R = 0.050$ and $R_w = 0.045$. All calculations were performed with the SHELXTL PLUS program package.

(7) Spectra were obtained with Chemagnetics CMC 300 (74.9 MHz) and MS 100 (25 MHz) CP-MAS NMR spectrometers. Spinning rates were adjusted to avoid interference between side bands and genuine signals. A 75 MHz spectrum of **1a** (β-form) at 90 °C was obtained for us by Beth Crockett and Paul Ellis of the University of South Carolina, and we express our gratitude to them.

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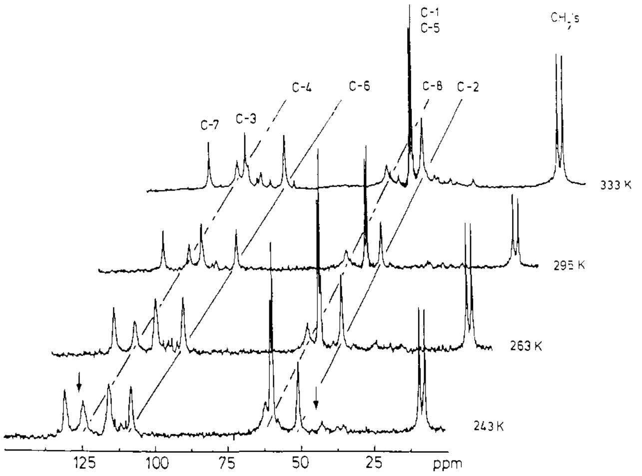
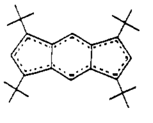


Figure 3. 74.9 MHz CP-MAS ^{13}C spectra of the α-form of **1a**. The arrows indicate the estimated limiting chemical shifts for C(6) and C(2).

tomerism can be calculated from the separation in chemical shifts for the pairs of exchange related carbon atoms and their limiting separation in the absence of exchange. In the case of the 3,7-dicarbonitrile (**1b**), the limiting separation is known from solution data[10] for temperatures at which the exchange is slow on the NMR time scale. For the 2,6-isomer, the separations have been estimated from ^{13}C chemical shift data for its 4-bromo derivative which exists as a single valence tautomer.[2] The values of ΔH and ΔS, calculated from K_{eq} vs T data, for these systems are presented in Table I. In these systems, the intermolecular forces on the semibullvalene molecule in the crystal evidently result in small differences in enthalpies and entropies for the two valence tautomers. In all three examples, both ΔH and ΔS are positive, and in the case of the β-form of **1a** their values lead to degeneracy (ΔG = 0) at room temperature.

The most important feature of this study derives from the comparison of the conclusions drawn from the results of the X-ray crystallography and solid-state ^{13}C NMR spectroscopy. The latter unequivocally establish the existence of rapidly equilibrating valence tautomers, whereas the former appear to favor the existence of structures intermediate between the exchanging forms. In the light of the NMR evidence, the temperature dependences of the 2–8 and 4–6 internuclear distances in the 3,7-dicarbonitrile is, of course, readily rationalized in terms of equilibrating valence tautomers, and, in fact, estimates of the equilibrium constants based on the observed and limiting internuclear distances for both the 3,7- and 2,6-isomers are in fair agreement with those obtained from the NMR data (Table I). X-ray analysis can distinguish between a pair of rapidly equilibrating valence tautomers and an intermediate structure, but only if it is based on large, low-temperature data sets and if it includes a very careful consideration of anisotropic displacement parameters.[11] Such treatments are exemplified by the recent X-ray diffraction studies of tetra-*tert*-butylcyclobutadiene,[12] tetra-*tert*-butyl-s-indacene, **2**,[13] and a series of transition-metal carbonyl clusters.[14] Solid-state ^{13}C NMR spectroscopy, however, appears to offer an attractive method for solving many problems concerning valence tautomerism in systems, such as the methano[10]annulenes, **3**,[15] barbaralanes (e.g., **4**),[16] and other semibullvalenes,[3,4] for which the less detailed X-ray structural analyses do not allow distinction between classical and intermediate structures.



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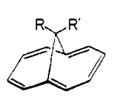

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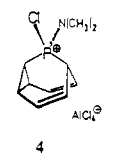

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Table I. Internuclear Distances (R_{ij}),[a] Equilibrium Constants ($K_{eq}{}^{K}$), and Thermodynamic Parameters for the Valence Tautomerism of **1a** and **1b**[h]

		1a		
		α-form	β-form	**1b**
$R_{2,8}$ (pm)		172.2[b]	199.0	183.5[c] 170.6[c,d]
$R_{4,6}$ (pm)		224.9[b]	199.6	204.8[c] 218.6[c,d]
$K_{eq}{}^{295}$	(NMR)	0.25	1.0	0.60
	(X-ray)[e]	0.2	1.0	0.6
$K_{eq}{}^{173}$	(NMR)			0.37[f]
	(X-ray)[d]			0.2
ΔH (kJ mol^{-1})		3.5 ± 0.1[g]	0.98 ± 0.02[g]	1.87 ± 0.03
ΔS (J mol^{-1} K^{-1})		0.3 ± 0.3[g]	3.4 ± 0.1[g]	2.1 ± 0.1

[a] None of these has been corrected for molecular librations. [b] Reference 2. [c] Reference 3a. [d] At 173 K. [e] The limiting values for the internuclear distances R_{ij}, used are $R_{2,8}$ = 158; $R_{4,6}$ = 235 pm.[2] [f] Extrapolated from K_{eq} vs T data. [g] Calculated from $\delta_{C(6)}-\delta_{C(2)}$. [h] K_{eq} = [high-temperature species]/[low-temperature species].

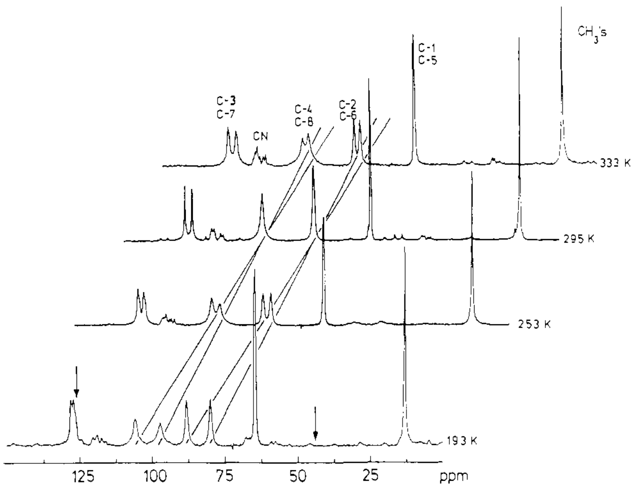

Figure 4. 74.9 MHz CP-MAS ^{13}C spectra of the β-form of **1a**. The arrows indicate the estimated limiting chemical shifts for C(6) and C(2).

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Supplementary Material Available: ^{13}C chemical shift data and equilibrium constants for α- and β-**1a** and **1b** and X-ray crystallographic data for β-**1a**, consisting of tables of atomic coordinates, anisotropic displacement parameters, internuclear distances, and bond angles (4 pages). Ordering information is given on any current masthead page.

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(10) We thank Prof. K. Müllen, Mainz for these values.

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