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Perturbation of Degeneracy of the Cope Rearrangement by the Crystal Lattice of the β-Form of 1,5-Dimethylsemibullvalene-2,6-dicarbonitrile As Studied by Variable-Temperature Solid-State Carbon-13 Spectroscopy and X-ray Crystallography at Cryogenic Temperatures

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Abstract: X-ray crystallographic structures of two polymorphs (α- and β-forms) of 1,5-dimethylsemibullvalene-2,6-dicarbonitrile, in which the molecules undergo rapid, nondegenerate Cope rearrangement, have been obtained over the temperature range 20−295 K. CP-MAS carbon-13 NMR spectra of the β-form have been observed over the temperature range 140−340 K. A generalized treatment for the perturbation of degeneracy has been developed and it is shown that the results of the X-ray and NMR methods are in excellent agreement. The thermodynamic parameters, ΔH^{p} and ΔS^{p}, for the perturbation of degeneracy in the β-form are reported. A possible explanation for the difference in the magnitudes of the perturbation of degeneracy in the two crystalline forms is suggested. It is noted that for equilibrating systems, for which the barriers for interconversion are of the order of 1−10 kJ mol^{-1}, the transition between rapid and extremely slow equilibration occurs over a very narrow range at cryogenic temperatures, thus precluding direct observation of limiting structures.

Introduction

A number of semibullvalenes[1,2] and barbaralanes[3,4,5] that undergo degenerate Cope rearrangements in solution have been studied by X-ray crystallography. Most X-ray diffraction analyses have been performed at a single temperature (room temperature), a number revealing anomalous internuclear distances, particularly between C2 and C8 of the cyclopropane ring and between the nonbonded atoms C4 and C6. Only a few variable-temperature studies have been reported. The results of the latter fall into two categories. The first embraces those systems whose apparent internuclear distances do not change with temperature, viz. tetramethyl barbaralane-2,4,6,8-tetracarboxylate[5] and 2,4,6,8-tetraphenylbarbaralane.[4b] This type forms well-ordered solid phases in which the Cope rearrangement is "frozen" as a result of intermolecular interactions in the crystal lattice. Thus only one of the two possible valence tautomers exists in the crystal, and the measured internuclear distances may hence be considered as good approximations for those of single molecules in solution and the gas phase.

The apparent internuclear distances of the semibullvalenes that belong to the *second*, more intriguing category, viz. 1,5-dimethylsemibullvalene-3,7-dicarbonitrile[6] and 1,5-dimethylsemibullvalene-2,4,6,8-tetracarboxylic anhydride,[2b] vary with the temperature. Their apparent internuclear distances C2−C8 decrease at lower temperatures while the apparent distances C4···C8 increase. A 9,10-dihydro-9,10-diazabullvalene[7] should be included in this group.

1,5-Dimethylsemibullvalene-2,6-dicarbonitrile (**1**) occupies a unique place among the systems that undergo extremely fast degenerate Cope rearrangements in solution because it crystallizes in two different but similar monoclinic modifications,

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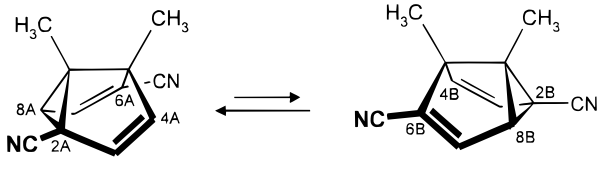
termed α- and *β*-forms.[8,9] Both share the same number of molecules in the unit cell ($Z = 4$) and the space group No. 14 ($P2_1/n$ and $P2_1/a$, respectively), but differ in the apparent internuclear distances. Variable-temperature carbon-13 74.9 MHz CP-MAS spectra unequivocally established a dynamic disorder associated with rapidly equilibrating *nonequivalent* valence tautomers for both modifications. This phenomenon has been first reported for the parent semibullvalene by Yannoni. No X-ray structure was, however, available for the solid phases of semibullvalene investigated.[10]



1A **1B**

Here we report an extended variable-temperature solid-state carbon-13 study, and the crystal and molecular structures of the two forms of **1** in the temperature range 20−295 K. The results of both methods are interpreted in terms of a model consisting of rearranging valence tautomers that occupy two different, exchanging sites in the crystal lattice. The perturbations of degeneracy by the crystal lattice, as expressed by the thermodynamic parameters ΔH^{P} and ΔS^{P} for these skewed equilibria between the valence tautomers, are calculated from both sets of experimental data.

We have shown that crystalline 1,5-dimethylsemibullvalene-2,6-dicarbonitrile (**1**) can exist as two polymorphs, α-**1** and *β*-**1**, which are readily distinguished by their carbon-13 CP-MAS spectra.[9] The spectrum of the α-form at room temperature resembles that of a nonexchanging semibullvalene, albeit one with somewhat anomalous chemical shifts for C2, C4, C6, and C8. In contrast, the room-temperature spectrum of the *β*-form corresponds either to a molecule undergoing a rapid, degenerate Cope rearrangement or to one possessing a symmetric (C_2), homoaromatic structure. The structure obtained by X-ray crystallography at room temperature is consistent with either possibility. However, carbon-13 spectra at other temperatures clearly show that the semibullvalene is, in fact, undergoing a rapid Cope rearrangement, which is "accidentally" degenerate at room temperature. The apparent equality of the C2−C8 and C4−C6 internuclear distances presumably has the same origin.

The anomalous C2−C8 and C4−C6 distances found at room temperature in the systems mentioned above are thus explained as arising from perturbation of a rapid, degenerate Cope rearrangement resulting from an unsymmetrical environment in the crystalline phase. If this is so, variable-temperature X-ray crystallography and solid-state carbon-13 NMR spectroscopy should, in general, yield the same value for the magnitude of the perturbation. This is best expressed in terms of the thermodynamics of the equilibrium between the valence tautomers. The *β*-form of **1** provides an ideal system for testing this hypothesis, because the barrier for the Cope rearrangement is very low and the equilibrium constant, which is approximately unity at room temperature, can therefore be determined over a wide temperature range by both methods. Such a test is particularly desirable because each method involves assumptions regarding the values of properties (δ's and r's) in the absence of exchange.

Before presenting the results of these studies, we provide a general treatment for assessing the magnitude of a perturbation in a rapidly rearranging, degenerate two-component system, which is applicable to both properties as well as any other that is a function of a perturbation of such systems.

Results

General Equations for the Perturbation of Degeneracy. Consider a general property X of an equilibrating two-component system $\mathbf{A} \rightleftharpoons \mathbf{B}$ that is degenerate in the absence of a perturbation. This exchange process interconverts features i of **A** and j of **B**. The mixture of the two components is defined by eq 1 where $f_{\mathbf{A}}$ and $f_{\mathbf{B}}$ are the fractions of the two components **A** and **B**.

$$f_{\mathbf{A}} + f_{\mathbf{B}} = 1 \tag{1}$$

$X_{\mathbf{A}}{}^{i}$ is the value of a property of a certain feature i of **A** that is converted to the value $X_{\mathbf{B}}{}^{j}$ of feature j of **B** through the exchange process. The time-averaged values are given by

$$\bar{X}_{i,j} = f_{\mathbf{A}} X_{\mathbf{A}}{}^{i} + f_{\mathbf{B}} X_{\mathbf{B}}{}^{j} \tag{2}$$

$$\bar{X}_{j,i} = f_{\mathbf{A}} X_{\mathbf{A}}{}^{j} + f_{\mathbf{B}} X_{\mathbf{B}}{}^{i} \tag{3}$$

Assuming that the perturbation has no effect on the values X^i and X^j of the properties of identical features in both molecules **A** and **B**, other than through exchange, one obtains the *difference* between the time-averaged values by eq 4.

$$\Delta X^{\mathrm{P}} = \bar{X}_{i,j} - \bar{X}_{j,i} = (f_{\mathbf{A}} - f_{\mathbf{B}})(X^i - X^j)$$

$$\Delta X^{\mathrm{P}} = (f_{\mathbf{A}} - f_{\mathbf{B}})\Delta X \tag{4}$$

The measured consequence of the perturbation is thus recognized as the difference ΔX^{P} between the two values $\bar{X}$ of the property that are time-averaged to equivalence in the absence of the perturbation. The limiting difference $\Delta X = X^i - X^j$ is the difference between those values in the absence of exchange. The *relative perturbation* is then defined as $\Delta X^{\mathrm{P}}/\Delta X$ and recognized as the difference between the fractions of the exchanging species (eq 5). In the special case of Saunders' isotopic perturbation method, it corresponds to what he terms "relative isotopic splitting".[11]

$$\frac{\Delta X^{\mathrm{P}}}{\Delta X} = f_{\mathbf{A}} - f_{\mathbf{B}} \tag{5}$$

Defining the equilibrium constant $K = [\mathbf{B}]/[\mathbf{A}]$ such that its value is less than unity at low temperatures, we obtain the relationship between the relative perturbation and the equilibrium constant (eq 6).

$$\frac{\Delta X^{\mathrm{P}}}{\Delta X} = \frac{1 - K}{1 + K} \tag{6}$$

The well-known temperature dependence of the equilibrium

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constant eventually affords eq 7, the nonlinear least-squares fitting of which to the $\Delta X^{\mathrm{P}}/\Delta X$ vs temperature yields the perturbation parameters ΔH^{P} and ΔS^{P} pertaining to the skewed equilibrium.

$$\frac{\Delta X^{\mathrm{P}}}{\Delta X} = \frac{1 - \exp\left(\frac{\Delta S^{\mathrm{P}}}{R} - \frac{\Delta H^{\mathrm{P}}}{RT}\right)}{1 + \exp\left(\frac{\Delta S^{\mathrm{P}}}{R} - \frac{\Delta H^{\mathrm{P}}}{RT}\right)} \tag{7}$$

Perturbation of Degeneracy by the Crystal Lattice As Measured by Variable-Temperature Carbon-13 CP-MAS Spectra. We reported a variable-temperature solid-state carbon-13 spectroscopic study of both α- and *β*-forms of **1** 10 years ago.[9] At that time, however, the available equipment only permitted a somewhat limited temperature range with considerable uncertainty regarding the actual temperatures, in particular at low temperatures. The acquisition of a more modern spectrometer with good temperature control and the availability of the lead nitrate technique for temperature calibration[12] encouraged us to repeat the earlier work. Data for the *β*-form of **1** have now been obtained in the temperature range 140−340 K. In the meantime, we have developed more realistic estimates for the shift differences in the absence of exchange.[13] The spectra of the region of interest are presented in Figure 1. The shift differences as a function of temperature are displayed in Figure 2.

In case of the NMR experiment, the general property X introduced above is the shift of a particular carbon-13 atom. Then ΔX^{P} corresponds to the crystal lattice induced splitting $\Delta\delta_{i,j}{}^{\mathrm{P}}$ of carbon-13 signals and $\Delta\delta_{i,j}$ is the estimated shift difference in the absence of exchange. Our current estimates of $\Delta\delta_{6,2}$ and $\Delta\delta_{4,8}$ are 76 and 84 ppm, respectively.[13] They have been based on the measured values for 2,6-barbaralanedicarbonitrile in the slow-exchange limit and an average correction term for the difference between substituted barbaralanes and 1,5-dimethylsemibullvalenes. The shift differences of Table 1, however, reveal that the values of the splittings $\Delta\delta_{6,2}{}^{\mathrm{P}}$ and $\Delta\delta_{4,8}{}^{\mathrm{P}}$ at each temperature are virtually the same over the whole range. This can only be true if the corresponding limiting shift differences $\Delta\delta_{6,2}$ and $\Delta\delta_{4,8}$ are also very similar. Therefore, we have set $\Delta\delta_{6,2}$ and $\Delta\delta_{4,8}$ equal to 80 ppm, the average of the two estimates. We also have explored the sensitivity of the ΔH^{P} and ΔS^{P} values to the parameters $\Delta\delta_{i,j}$ by performing the calculation using the values 75 and 85 ppm. An error of ±5 ppm in $\Delta\delta_{i,j}$ translates into an error of less than 7% in both ΔH^{P} and ΔS^{P} (Table 2 included in Supporting Information).

The major source of error in these experiments is associated with the determination of the true sample temperature. Limitations of the instrument time precluded the use of lead nitrate as an internal temperature standard. Therefore, the readout of the variable-temperature unit was calibrated with lead nitrate in a separate experiment.[12]

The C3/C7 signals should, of course, coincide at 285 K as observed for C2/C6 and C4/C8, whereas they only do so at 174 K. An intrinsic differential shift of 2.3 ppm added to the observed shift would bring the data into agreement with those observed for C4/C8 and C2/C6. We return to a possible origin of this anomaly below.

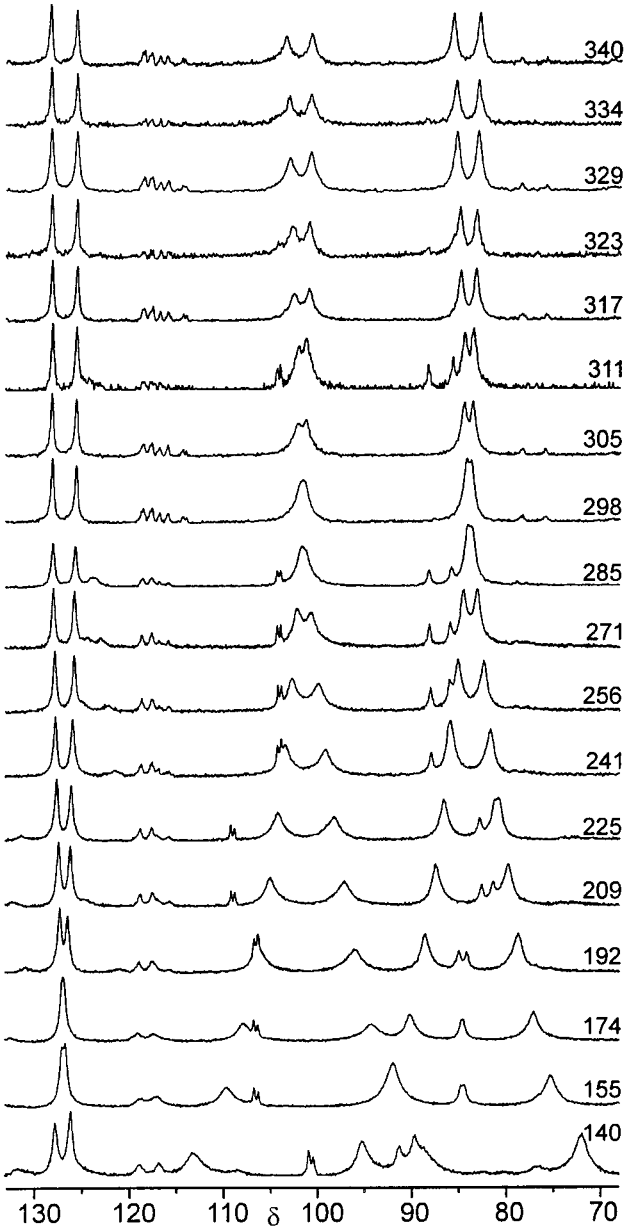

Figure 1. Partial carbon-13 100.6 MHz CP-MAS spectra of the *β*-form of **1** recorded in the temperature range 140−340 K.

X-ray Crystallography of the α- and *β*-Forms of 1,5-Dimethylsemibullvalene-2,6-dicarbonitrile in the Temperature Range 20−295 K. Complete dynamic disorder between two sites in the crystal is the crystallographic equivalent of perfect degeneracy in solution, which time-averages the various features of rearranging molecules. In the case of X-ray diffraction analyses, the general property X introduced above may be a certain molecular symmetry[14] or an internuclear distance $r_{i,j}$. The perturbation by the crystal lattice of the time-averaged equidistances between C2 and C8, and C4 and C6 of **1** is hence measured by the difference between these distances $\Delta r^{\mathrm{P}} = \bar{r}_{4,6} - \bar{r}_{2,8}$. Calculation of the relative perturbation (eq 5) requires knowledge or at least an estimate of the difference between these distances in a single nonrearranging valence tautomer. The X-ray crystallographic study at 20 K of the α-form provides this value.

X-ray diffraction analyses were performed for the α-form at three and for the *β*-form at eight different temperatures in the

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[14] ΔX would then measure the amount of distortion from that symmetry, for an example, see ref 15. In the case of **1**, the time-averaged molecular symmetry is C_2. For the sake of simplicity, however, we regard only the two interchanging intramolecular distances that are varied most strongly by the Cope rearrangement.

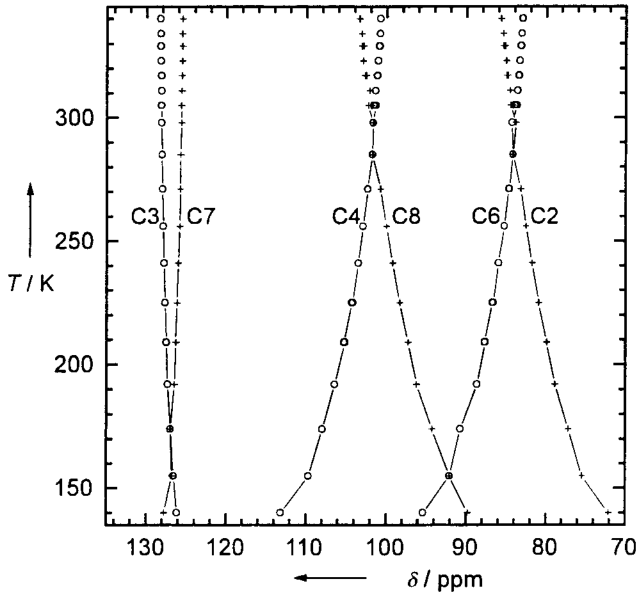

Figure 2. Plot of the apparent chemical shifts vs temperature for the carbon-13 atoms of β-**1** in the range 70−130 ppm.

Table 1. Crystal Lattice-Induced Splittings $\delta_{i,j}$ [ppm] in Variable-Temperature Carbon-13 CP-MAS Spectra of the β-Form of **1**

T [K]	$\Delta\delta_{6,2}^{\mathrm{P}}$	$\Delta\delta_{4,8}^{\mathrm{P}}$	$\Delta\Delta\delta^{\mathrm{P}}$	$\Delta\delta_{3,7}^{\mathrm{P}}$
340	−2.67	−2.60	−0.07	2.74
	−2.79	−2.70	−0.09	2.74
334	−2.34	−2.30	−0.04	2.70
329	−2.02	−1.98	−0.04	2.66
	−2.32	−2.24	−0.08	2.70
	−2.30	−2.26	−0.04	2.70
323	−1.75	−1.89	0.14	2.64
317	−1.37	−1.33	−0.04	2.56
	−1.36	−1.45	0.09	2.56
	−1.62	−1.60	−0.02	2.60
311	−0.96	−0.76	−0.20	2.52
	−0.96	−0.76	−0.20	2.52
305	−0.22	−0.28	0.06	2.44
	−0.46	−0.38	−0.08	2.47
	−0.40	−0.42	0.02	2.48
	−0.86	−0.92	0.06	2.54
298	0.46	0.00	0.46	2.48
285	0.00	0.00	0.00	2.32
271	1.42	1.62	−0.20	2.20
	1.52	1.60	−0.08	2.18
256	2.71	2.92	−0.21	2.03
241	4.22	4.29	−0.07	1.79
225	5.74	5.82	−0.08	1.50
	5.79	6.01	−0.22	1.50
209	7.84	8.00	−0.16	1.16
	7.70	7.89	−0.19	1.22
192	9.78	10.17	−0.39	0.81
174	13.57	13.66	−0.09	0.00
155	16.62	17.61	−0.99	−0.20
140	23.27	23.35	−0.08	−1.62

range 20−295 K. For α-**1,** the room-temperature structure reported by Quast et al.[8] was used as an initial model in the refinements, which ran routinely to convergence at all three temperatures. Normal atomic displacement parameters were observed down to 20 K, with no indication for a similar disorder as for the β-form (see below). The molecular asymmetry already observed at room temperature[8] becomes somewhat more pronounced at 20 K in that $\bar{r}_{2,8}$ decreases by 10.7 pm and $\bar{r}_{4,6}$ increases by 8.3 pm.

The room-temperature data of the β-form reported by Jackman et al.[9] were used for a re-refinement of the 295 K data set. Subsequently, the atomic positional and displacement parameters of a higher-temperature data set were taken as input for the next lower-temperature data.

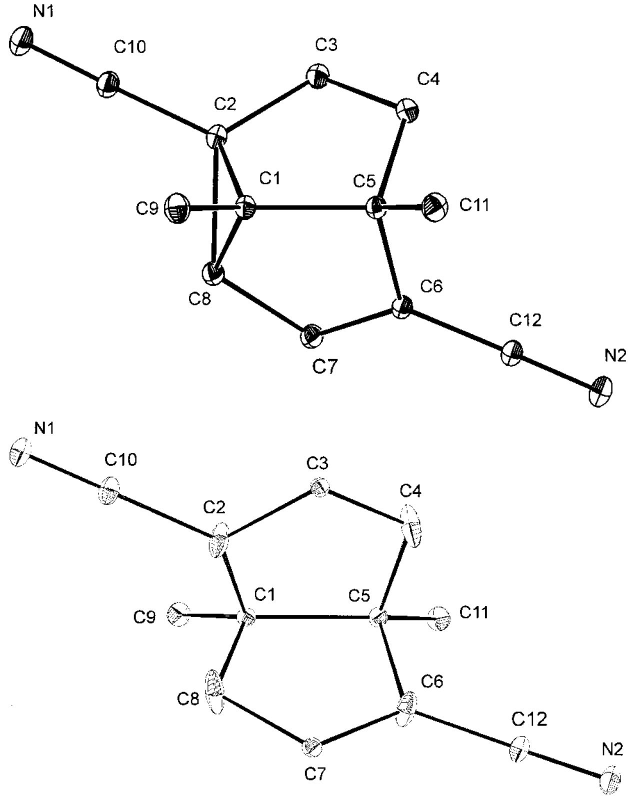

Figure 3. ORTEP representation of the α- (above) and β-forms of **1** (below, disorder not considered) at 20 K. The displacement ellipsoids are drawn at a 50% probability level.

Conventional full matrix least-squares refinements minimizing the quantity $\sum w(F_o - k|F_c|)^2$ with $w = 1/\sigma^2(F_o)$ were executed using the SFLSX link of the XTAL2.2 program system.[16] Anisotropic (for C and N) and isotropic (for H) displacement parameters were used in the refinement, which ran smoothly to convergence at all temperatures yielding agreement factors as listed in Table 4 included in the Supporting Information.

The distances $\bar{r}_{2,8}$ and $\bar{r}_{4,6}$ at various temperatures are compiled in Table 2. Lists of the crystal data and experimental details, the $U_{i,j}$'s for C2 and C4, and the ORTEP representations at 295 K are included in the Supporting Information. The ORTEP representations at 20 K are displayed in Figure 3. Plots of the apparent internuclear distances $\bar{r}_{2,8}$ and $\bar{r}_{4,6}$ vs temperature are shown in Figure 4.

The apparent molecular geometry of β-**1** changed from the seemingly symmetric structure at room temperature to an asymmetric one at 20 K. The largest difference between $\bar{r}_{2,8}$ and $\bar{r}_{4,6}$ was observed at 50 K. Inspection of Figure 3 reveals that the anisotropic displacement parameters, especially those for the critical two-atom pairs C2/C8 and C4/C6, tend to unusual values with decreasing temperature suggesting a disorder at these sites. At this stage of refinement, we already had the 20 K structure of the α-form at hand (Figure 3 above), which showed no unusual properties of any displacement parameters. A rigid body analysis[17] confirmed these findings. The anisotropic

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Table 2. Selected Apparent Internuclear Distances $\bar{r}_{i,j} = C_i - C_j$ [pm] for the α- and *β*-Forms of **1** in the Temperature Range 20−295 K

	T [K]	$\bar{r}_{2,8}$	$\bar{r}_{4,6}$
α-**1**	295	173.5(6)	226.2(6)
	85	164.4(3)	234.3(3)
	20	162.8(1)	234.5(1)
β-**1**	295	199.9(4)	199.6(4)
	200	195.3(3)	203.1(3)
	120	186.3(3)	210.5(3)
	85	180.3(3)	217.5(3)
	65	176.8(3)	221.2(3)
	50	175.5(3)	221.8(3)
	35	180.9(3)	217.3(3)
	20	182.1(4)	215.5(4)

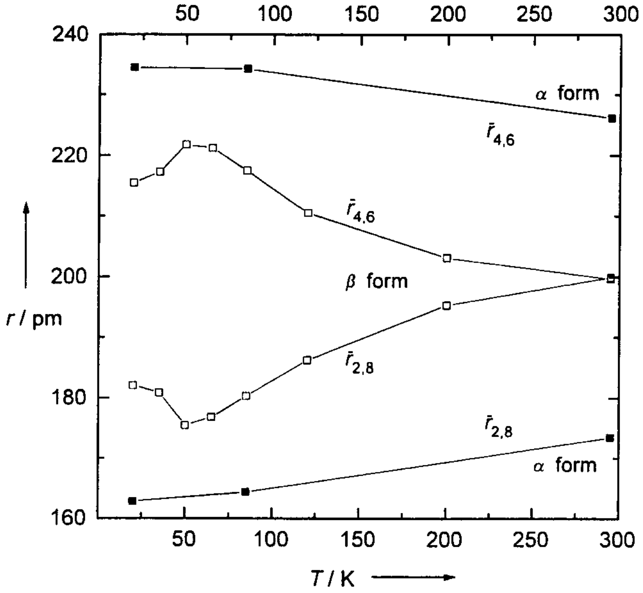

Figure 4. Temperature dependence of the apparent internuclear distances $\bar{r}_{2,8}$ and $\bar{r}_{4,6}$ [pm] for the α- (filled squares) and *β*-forms of **1** (hollow squares). Disorder is not considered for the *β*-form.

displacement parameters (ADP's) predicted by the rigid-body motion model (calculated from the **T**, **L**, and **S** tensors) were subtracted from those observed and the residuals, $\Delta U = U(\text{exp}) - U(\text{TLS})$, were visualized with the use of the computer graphics program PEANUT[18] in terms of the residual root-mean-square displacement (RMSD) surfaces at each atomic site. In Figure 5, the solid/dotted lobes display directions along which the rigid-body model under-/overestimates the atomic displacements with respect to the observed ADP's. For the α-form, the U_{ij}'s are almost completely described by the rigid-body model, which is not true for the *β*-form. We conclude that disorder plays no recognizable role in the α-**1** crystal structure but is obvious in *β*-**1**.

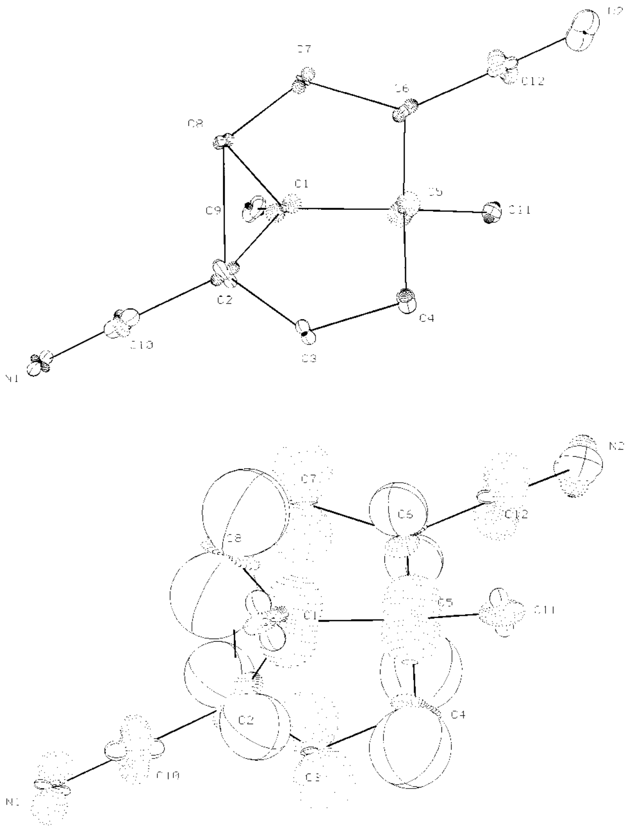

Figure 5. "Peanut" representation of the α- and *β*-forms of **1** at 20 K with respect to $\Delta U_{ij} = U_{ij}(\text{exp}) - U_{ij}(\text{TLS})$, see also text.

The observed apparent structures clearly are the statistical means weighted according to the relative thermal populations of the two valence tautomers separated in enthalpy by ΔH^{P}. The maximum of the difference between $\bar{r}_{2,8}$ and $\bar{r}_{4,6}$ of the *β*-form observed at 50 K (Figure 4) appears to indicate that disorder decreases down to this temperature and increases again on further cooling. We consider, however, this phenomenon as a striking demonstration of the limitations imposed by energy barriers on low-temperature investigations of equilibrating systems. In the absence of heavy-atom quantum-mechanical tunneling,[19−21] which is deemed unimportant in the present system because of the large internuclear distances involved,[22] the very low energy barriers, such as we are dealing with here, may cause the lifetimes of the equilibrating species to vary by many powers of 10 over just a few degrees of temperature (Figure 6). This renders impossible the observation of a thermally equilibrated system at very low temperatures within experimentally accessible periods of time. The particular values of the internuclear distances found for the *β*-form below 65 K probably depend on the rate at which the sample was cooled. Therefore, further consideration of these values is not warranted. In principle, the same line of reasoning holds also for the α-form, of course. Because α-**1** is, however, much more ordered than *β*-**1** already at room temperature, the apparent internuclear distances $\bar{r}_{2,8}$ and $\bar{r}_{4,6}$ change very little on cooling to 20 K (Figure 4), the temperature at which they may be regarded as representing the distances $r_{2,8}$ and $r_{4,6}$ in the limit of perfect order.

Discussion

Comparison of the Perturbation Parameters ΔH^{P} and ΔS^{P} obtained from X-ray Crystallography and Solid-State Carbon-

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[22] For tunnelling to occur at a significant rate, the displacements of the atoms must not be much greater than the de Broglie wavelengths of the atoms. A carbon atom, for example, with a kinetic energy of, say, 20 kJ mol^{-1} has a de Broglie wavelength of 18 pm,[19a] which is significantly smaller than the displacements involved in the Cope rearrangement of **1**, $\Delta r = r_{4,6} - r_{2,8} = 71.7$ pm (measured for α-**1** at 20 K).

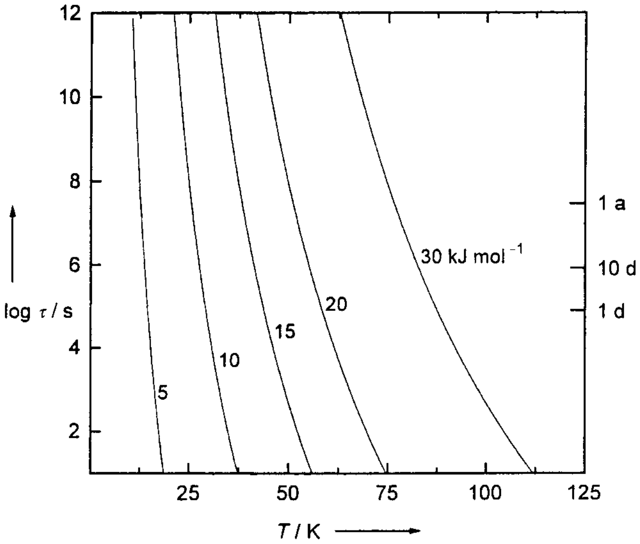

Figure 6. Temperature dependence of the lifetime τ for Arrhenius behavior in the absence of heavy-atom quantum-mechanical tunneling. The lifetimes τ were calculated from the various activation energies E_a given and a constant frequency factor $A = 10^{13}$ s^{-1} according to the equation $\log \tau = E_a/(RT \ln 10) - \log A$.

13 NMR Spectroscopy. The first determination of an energy difference between solid-state conformers by variable-temperature X-ray diffraction was reported by Simmons and co-workers more than 10 years ago.[15] A limited number of studies report the combined use of variable-temperature NMR and X-ray diffraction techniques to investigate solid-state reactions in more qualitative terms.[5,23] We are unaware, however, of such studies that are concerned with the *quantitative* evaluation of a solid-state phenomenon. The general equations for the perturbation of degeneracy derived above allow us to directly compare the data obtained by these two very different but complementary methods. Thus we may plot against temperature the relative perturbations $\Delta X^P/\Delta X$ on a common scale, where the general property X represents time-averaged chemical shifts of various carbon-13 atoms and time-averaged internuclear distances. Figure 7 displays such a plot for the β-form of **1**. Clearly the agreement between the two disparate methods is very satisfactory.

Equation 7 has been fitted by the method of nonlinear least squares to the relative perturbation vs temperature for the separate and combined data sets to afford values of the perturbation parameters ΔH^P and ΔS^P presented in Table 3 together with the squares of the correlation coefficients. The values for these parameters agree within 14%. The same treatment of the data from our earlier measurements of $\Delta\delta_{i,j}$, which were performed for β-**1** over a more limited temperature range, also gave reasonable agreement. We believe that a major source of errors in these parameters is the precision with which the actual NMR sample temperatures are known.

Possible Origins of the Perturbation of Degeneracy for α- and *β*-1. Inspection of the intermolecular distances in the α- and β-forms reveals that the only close interactions are between the nitrogen atoms and the hydrogen atoms at C3 and C7. These intermolecular distances are summarized in Table 4 and shown in Figures 8 and 9. We note that the interactions appear more severe in the β-form in that both the C3 and C7 hydrogens are involved in H- - -N contacts below 300 pm, and are almost certainly the cause of the apparent intrinsic contributions to chemical shifts between C3 and C7, to which we drew attention in our discussion of the carbon-13 spectra of the β-form. No such chemical shift anomaly is observed for the α-form,[9] for which the splittings of C3/C7 signals increased

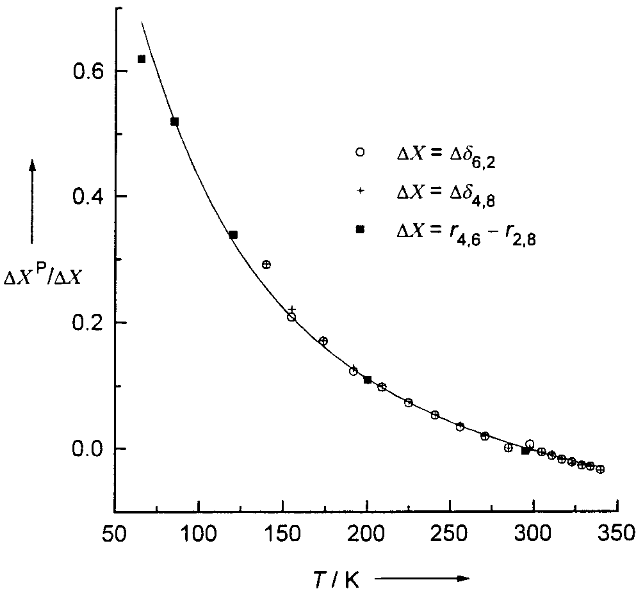

Figure 7. Diagram of the crystal lattice-induced relative perturbation of degeneracy $\Delta X^P/\Delta X$ vs temperature obtained for β-**1** from carbon-13 CP-MAS spectra ($\Delta X = \Delta\delta_{i,j}$) and X-ray diffraction analyses ($\Delta X = r_{4,6} - r_{2,8}$). The curve is a nonlinear least-squares fit of eq 7 to the combined data sets.

Table 3. Perturbation Parameters ΔH^P and ΔS^P for the β-Form of **1** Obtained by Fitting with the Nonlinear Least-Squares Method of Eq 7 to the Separate and Combined Sets of $\Delta X^P/\Delta X$ vs Temperature

data set ΔX^P	T [K]	ΔH^P [J mol^{-1}]	ΔS^P [J mol^{-1} K^{-1}]	r^2 [a]
$\Delta\delta_{6,2}{}^P$ [b]	140−340	1222.4 ± 18.5	4.167 ± 0.073	0.99391
$\Delta\delta_{4,8}{}^P$ [b]	140−340	1247.0 ± 15.0	4.241 ± 0.059	0.99617
$\Delta\delta_{6,2}{}^P$ [c]	193−363	997.5 ± 23.5	3.432 ± 0.091	0.99807
$\Delta\delta_{4,8}{}^P$ [c]	193−333	1028.0 ± 22.6	3.511 ± 0.090	−[d]
Δr^P	65−295	1066 ± 62	3.45 ± 0.51	0.99199
$\Delta\delta_{6,2}{}^P + \Delta\delta_{4,8}{}^P + \Delta r^P$ [b]	65−340	1146.0 ± 14.7	3.874 ± 0.063	0.99267

[a] Square of the correlation coefficient. [b] $\Delta\delta_{i,j}{}^P/\Delta\delta_{i,j}$ of the present study. [c] $\Delta\delta_{i,j}{}^P/\Delta\delta_{i,j}$ of the earlier study[9] recalculated with the limiting value $\Delta\delta_{i,j} = 80$ ppm. [d] The number of data did not permit the calculation of r^2.

Table 4. Short Intermolecular Distances (<350 pm) in the α- and β-Forms of **1** As Measured by X-ray Crystallography at 295 K

	Intermolecular distance	[pm]
α-**1**	C3—H- - -N2	300
	C3—H- - -N2	344
	C7—H- - -N2	319
	C7—H- - -N1	264
β-**1**	C3—H- - -N1	288
	C3—H- - -N1	263
	C7—H- - -N2	259

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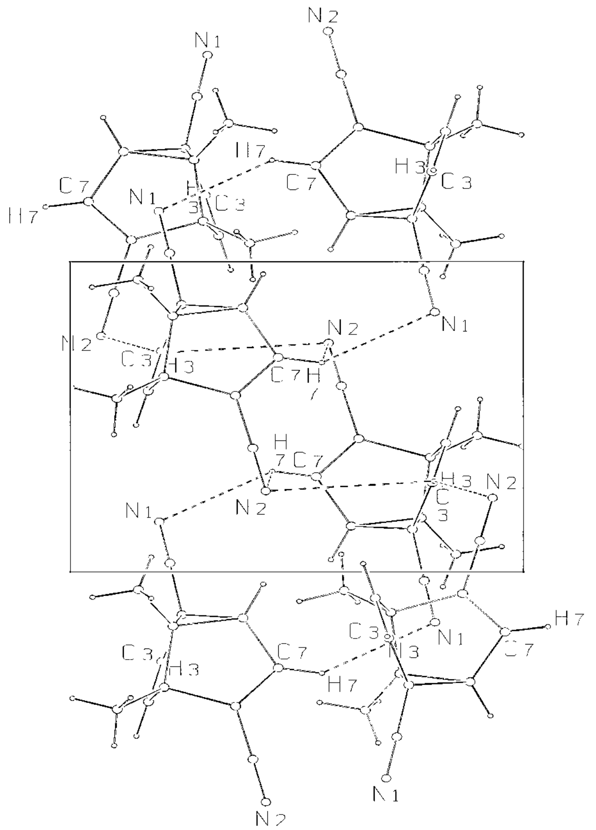

Figure 8. Picture of the packing of α-**1** in the *b,c* plane showing short distances between hydrogen and nitrogen atoms (<350 pm).

monotonically with the decreasing temperature in line with the behavior of the C2/C6 and C4/C8 resonances: Just how these close interactions of the nitrile groups affect the subtle interplay between ΔH^{p} and ΔS^{p} in the two polymorphs cannot at present be rationalized.

Conclusions

Both the X-ray and the solid-state ^{13}C NMR are useful methods for quantitative studies of the perturbation of degeneracy. The success of the study of β-**1** is, however, somewhat fortuitous because experimental values for $r_{2,8}$ and $r_{4,6}$ in the absence of disorder are available from an X-ray diffraction study of the α-form at temperatures for which it was apparent that no disorder prevailed. In general, it may not be possible to obtain limiting values for the absence of exchange, because, as pointed out above, the barriers to exchange are low enough and the free energy differences between the two valence tautomers are small so that it becomes impossible to reach the completely ordered state, and thus one has to rely on estimated values. Incidentally, it was not possible to evaluate ΔX together with ΔH^{p} and ΔS^{p} using three-parameter optimization (eq 7). Evidently, a larger and more accurate data set would be required.[24]

These studies obviously can be extended to other semibullvalenes, barbaralanes, and related 2-fold degenerate systems for which X-ray studies at room temperature have indicated perturbation of degeneracy in the solid state.[1-3,6,7] We can recognize two categories of perturbations of degeneracy, namely, by intra- and intermolecular interactions. *Intra*molecular perturbations may arise from isotopic substitution,[11,25,26] substituents, monoannelation,[8,13,26-34] or heteroatoms.[35] These perturbations can be studied by NMR spectroscopy. If the exchange is slow on the NMR time scale, the two valence tautomers can be directly observed. In the case of rapid exchange, the method of Saunders is applicable.[11] Perturbations that have an *inter*molecular origin such as in the case studied can be observed only if the molecule persists in the perturbing environment for a time that is long compared with the time scale of the particular experiment. Other sources of anisotropic environments which might satisfy this condition include inclusion compounds,

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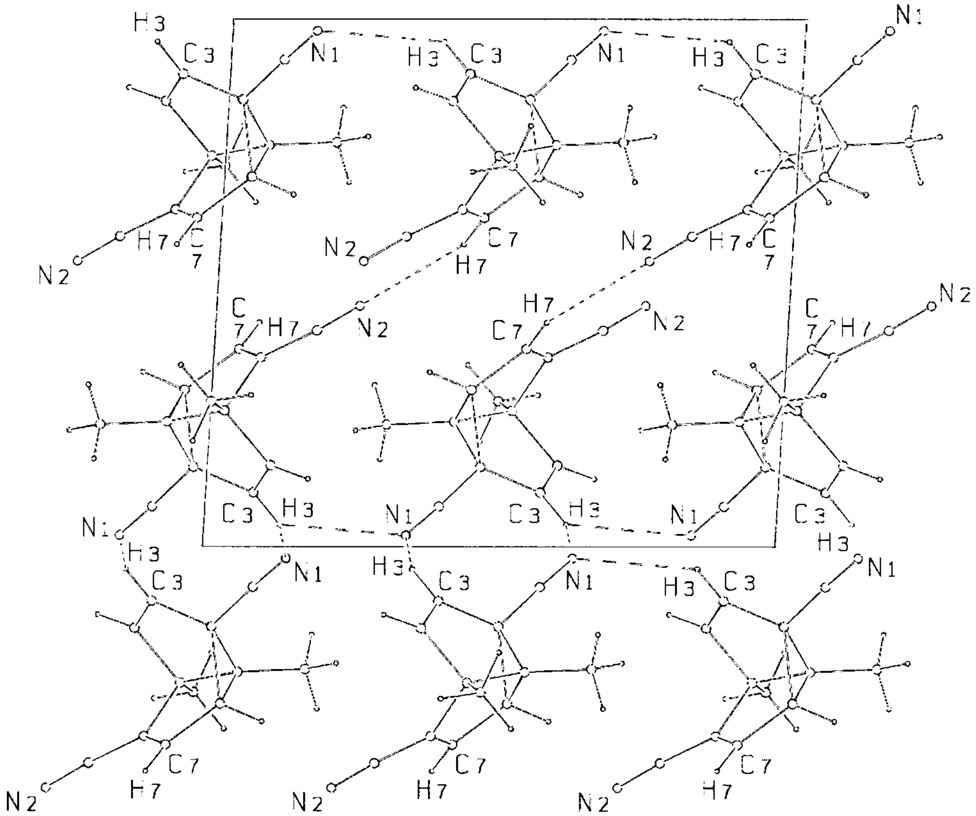

Figure 9. Picture of the packing of β-**1** in the *a,c* plane showing short distances between hydrogen and nitrogen atoms (<350 pm).

supramolecular cavities, e.g. zeolites, and even, perhaps, surfaces. An extension of studies such as this could include the effects of pressure, electric fields, etc., on the magnitudes of the perturbations of degeneracy.

Finally, we note that only those properties that are associated with a particular feature of the molecule can be used to probe the perturbation. Global properties such as light absorption cannot be used for these studies.

Experimental Section

1,5-Dimethylsemibullvalene-2,6-dicarbonitrile (**1**) was prepared according to the improved procedure.[36] Mainly β-**1** was obtained by rapid distillation on a rotary evaporator of the solvent from a solution of **1** in petroleum ether (boiling range 30−75 °C)/ethyl acetate (85:15). The solid-state carbon-13 spectrum of the crude product indicated the presence of small amounts of α-**1**. Recrystallization from ethyl acetate by cooling the solution slowly to −35 °C yielded yellow prismatic crystals of β-**1** that were suitable for X-ray crystallography. Pale yellow crystals of the α-form were prepared as described.[8]

The X-ray experiments were executed in the same way for the α- and β-forms. Crystals were fixed with Araldite glue on a special low-temperature mounting described previously.[37] X-ray measurements were executed with a large Huber four-circle diffractometer (400 mm diameter, type 5042) with offset χ circle equipped with a double-stage He refrigerator (Displex DE 202) and a Be vacuum chamber around the cold head.[38] Crystal alignment was first controlled optically, and later, when the specimen was hidden from view inside the Be chamber, by X-ray diffraction via the "C8 routine".[39] The temperature was measured with an Au(Fe)/chromel thermocouple fixed in a small hole at the tip of the second stage and was calibrated via a Si diode, fixed close to it. Temperature could be kept constant better than 0.5 K for weeks. For all experiments, Nb-filtered Mo Kα radiation was used at 50 kV and 40 mA. After a measurement at room temperature, the crystals were cooled maintaining a temperature decrease of 0.6 K min^{-1}. At each of the low temperatures, at which data collection was intended, the crystal position and orientation as well as the lattice parameters were redetermined by centering 50 high-order reflections. At each temperature, intensity data were collected in the $\omega-2\theta$-scan mode including intensity profile recording. Except for the lowest temperature, $2\theta_{\max}$ was set to 55°. At 20 K, high-order data were measured up to $2\theta = 104°$, to permit a detailed analysis. Three standard reflections were measured every 90 min, showing in no case a significant variation. In addition to the usual Lp-correction, an analytical absorption correction was applied to obtain the path lengths for extinction refinement. For further details of data collection see Tables S3 and S4 included in the Supporting Information.

Variable-temperature carbon-13 100.6 MHz CP-MAS spectra were recorded on a Bruker DSX 400 NMR spectrometer. The Bruker variable-temperature unit BVT 3000 was calibrated at 11 temperatures over the range 136−294 K with a lead nitrate sample.[12] The nominal temperatures, which were read off from the variable-temperature unit, were then fitted by a second-order polynomial to the true (lead nitrate) temperatures (square of the correlation coefficient = 0.9996):

$$T[\mathrm{Pb(NO_3)_2}] = 31.486 + 1.1286T_{\mathrm{nom.}} - 0.0008T_{\mathrm{nom.}}^{\;2}$$

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Supporting Information Available: ORTEP representation of the α and the β-form of **1** at 295 K (Figure S1); chemical shifts in carbon-13 CP-MAS spectra of β-**1** (140−340 K, Table S1); results of the nonlinear least-squares fitting of eq 7 to the $\Delta\delta_{i,j}^{P}/\Delta\delta_{i,j}$ vs temperature using estimated shift differences in the absence of exchange, $\Delta\delta_{i,j} = 75$, 80, and 85 ppm (Table S2); crystal data and experimental conditions for α-**1** and β-**1** (20−295 K, Tables S3 and S4); and molecular data of α-**1** and β-**1** (20−295 K, Table S5) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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