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APPLICATIONS OF CARBON-13 RESONANCE SPECTROSCOPY—XV[a]

THE DEGENERATE COPE-REARRANGEMENT OF BULLVALENE

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Abstract—The temperature dependence of the ^{13}C-NMR spectrum of bullvalene has been studied from −67 to +128°C using fourier transform spectroscopy and ^{1}H broadband decoupling. Lineshape analysis based on the Anderson-Kubo-Sack theory yielded $E_a = 13{\cdot}9 \pm 0{\cdot}1$ kcal/mole, $\log A = 14{\cdot}0 \pm 0{\cdot}1$, $\Delta H\ddagger = 13{\cdot}3 \pm 0{\cdot}1$ kcal/mole, and $\Delta S\ddagger = 3{\cdot}4 \pm 0{\cdot}4$ e.u. The pertinent features of dynamic ^{13}C-NMR spectroscopy are discussed.

INTRODUCTION

Though the majority of dynamic phenomena occurring in organic molecules has been detected and measured by NMR spectroscopy in recent years,[1] carbon-13 NMR spectroscopy was used relatively seldom for this purpose. With the introduction of pulse fourier transform (PFT) NMR spectroscopy[2,3] this situation has begun to change, since satisfactory ^{13}C-NMR spectra may now be obtained in relatively short time. Furthermore, there are several attractive features connected with the use of ^{13}C instead of ^{1}H dynamic NMR spectroscopy. ^{13}C-{^{1}H}-spin decoupling usually yields simple two sites problems where lineshape analysis is straight-forward.[4] In addition, in many cases several of such two sites exchange systems are present that permit crosschecks of the experimental information. Finally the larger chemical shifts observed for exchanging carbon nuclei allow the determination of still smaller energy barriers, because the slow exchange limit is more easily accessible.† Since the equivalence of continuous wave and PFT results has been secured by theoretical considerations for intramolecular processes,[5] ^{13}C-NMR promises to be a valuable tool for kinetic studies in the field of fast, reversible first order rate processes.

On the other side—apart from the usual difficulties met in dynamic NMR spectroscopy that are well known today[6,1]—certain features that may introduce systematic errors into the results obtained from ^{13}C-PFT-NMR spectroscopy have to be discussed. Differences in spin lattice relaxation times (T_1) and different Overhauser enhancement factors[7] usually yield erroneous integration data for different types of ^{13}C-NMR signals, unless special techniques are used to circumvent these shortcomings. The "population" of the various sites does, therefore, only rarely correspond to the true mole fractions. In addition, the T_1-values are temperature dependent.[8] Secondly, the various experimental settings possible in PFT spectroscopy for pulse width, sampling rate, delay time etc as well as phase errors may influence the lineshape significantly. Indeed, there have already appeared reports on the activation enthalpy for the ring inversion of *cis*-1,2-dimethylcyclohexane that differ by nearly 30%.[9,10] On the other hand, Gansow *et al.*[11] found good agreement between ^{1}H- and ^{13}C-NMR data for a simple two sites process with equal populations.

In order to get more information on the reliability of dynamic ^{13}C-PFT-NMR spectroscopy, we have undertaken a study of the degenerate Cope rearrangement of bullvalene (1) by this technique, using complete lineshape analysis for the determination of the activation parameters. The valence isomerization of bullvalene[12] was chosen for several reasons:

(1) A number of investigations using ^{1}H-NMR spectroscopy[13–15] have already led to a set of Arrhenius parameters E_a and A as well as to $\Delta H\ddagger$- and $\Delta S\ddagger$-values that may serve as a guideline for the criticism of the ^{13}C results.

(2) The spectral changes caused by the dynamic process extend over a fairly large temperature range (*ca* 160°), making the measurements more reliable.§

(3) Since exchange occurs between several sites, the lineshape is expected to be more sensitive to the rate constants than in simple two sites problems. To our knowledge lineshape analysis of ^{13}C spectra have sofar been confined to two sites problems mostly.

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[a] For part XIV see J. Prestien and H. Günther, *Angew. Chem.* **86**, 278 (1974); *Ibid.* Int. Ed. **10**, 276 (1974).

†The following paper uses ^{1}H-NMR for the measurement of a very low energy barrier for cyclohexanone: F.A.L. Anet, G. N. Chmurny and F. Krane, *J. Am. Chem. Soc.* **95**, 4423 (1973).

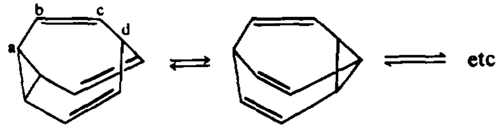
§This statement is based on the usual and hitherto unchallenged assumption of temperature independent activation parameters.

(4) The exchange occurs between sites of different hybridization and is thus more general than exchange processes observed for ring inversion or hindered internal rotation.

RESULTS

The ^{1}H-decoupled ^{13}C-NMR spectrum of bullvalene in the slow exchange limit (Fig 1) shows the expected four absorptions at $\delta = 20{\cdot}5$, $30{\cdot}0$, $127{\cdot}2$, and $128{\cdot}1$ ppm. Assignments for C_a and C_d follow immediately from the intensity ratio of the two lines at 20·5 and 30·0 ppm, that for C_b and C_c may be derived from the temperature dependence of the lineshape as discussed below.

The equivalence of all carbons of bullvalene in the fast exchange limit is a consequence of the degenerate Cope rearrangement that documents itself by a series of valence isomerizations of type $1 \rightleftharpoons 1' \rightleftharpoons$etc:



1 1'

The exchange pattern connected to each step is given by

$$C_a \rightleftharpoons C_d$$
$$2C_a \rightleftharpoons 2C_c$$
$$C_b \rightleftharpoons C_c$$
$$(2C_b \rightleftharpoons 2C_b)$$

and leads, within the framework for the Anderson-Kubo-Sack theory,[16] to the following expression for the spectral line-shape $I(\omega)$:

$$I(\omega) \sim \mathrm{Re}[p_a p_b p_c p_d]$$
$$\begin{bmatrix} \alpha_a + k & 0 & -\frac{2}{3}k & -\frac{1}{3}k \\ 0 & \alpha_b + \frac{1}{3}k & -\frac{1}{3}k & 0 \\ -\frac{2}{3}k & -\frac{1}{3}k & \alpha_c + k & 0 \\ -k & 0 & 0 & \alpha_d + k \end{bmatrix}^{-1} \begin{bmatrix} 1 \\ 1 \\ 1 \\ 1 \end{bmatrix} \tag{1}$$

where p_i is the mole fraction, k the rate constant, and

$$\alpha_i = i(\omega - \omega_i) + (1/T_2)_i \tag{2}$$

with ω as the variable frequency, ω_i as the resonance frequencies of the four sites and $(1/T_2)_i$ as the respective natural linewidths; (1) is fully equivalent to the equation valid for the ^{1}H-NMR spectrum.[13] A program based on equation (1) was written to allow for the preparation of plots using various k-values. Visual comparison of these plots with the experimental curves obtained at different temperatures was used to determine the k-values. Several examples of theoretical and experimental spectra are shown in Figs 2 and 3.

As is seen in Fig. 2, from the olefinic carbon resonances that at low field shows stronger exchange broadening than that at high field and may thus be assigned to C_c, since with one rearrangement all three carbons of this type change their environment whereas only one carbon of type b is affected. Transverse relaxation by magnetization transfer is, therefore, more effective in the first case leading to a larger linewidth.

1,1,2,2,-Tetrachloroethane proved to be a suitable solvent that allowed measurements over the whole temperature range from the slow to the fast exchange limit. In order to account for the temperature variations of the chemical shifts, five measurements between −67 and −28°C were performed the results of which are represented in Fig 4. A linear dependance of ν_i on the temperature

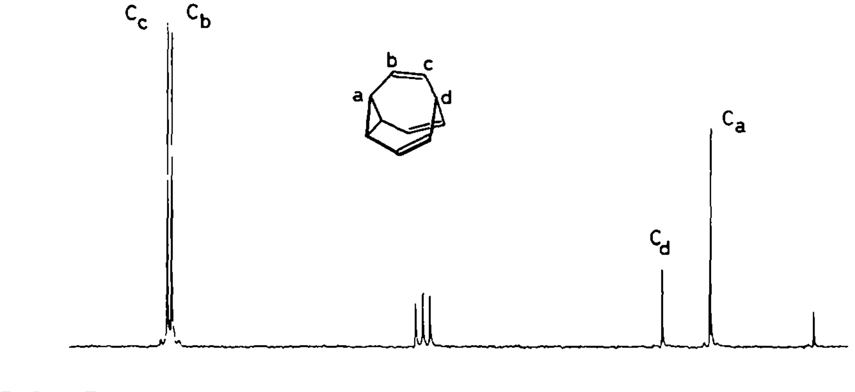


Fig 1. ^{13}C–PFT–NMR spectrum of bullvalene at −62°C; solvent $CDCl_3$, internal reference tetramethylsilane.

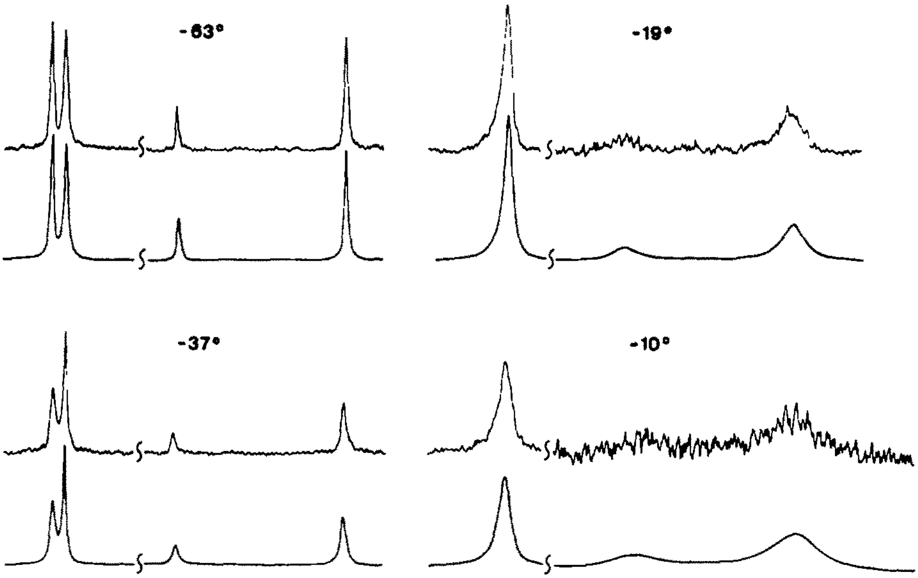


Fig 2. Observed and calculated ^{13}C-NMR spectra of bullvalene in the slow exchange region.

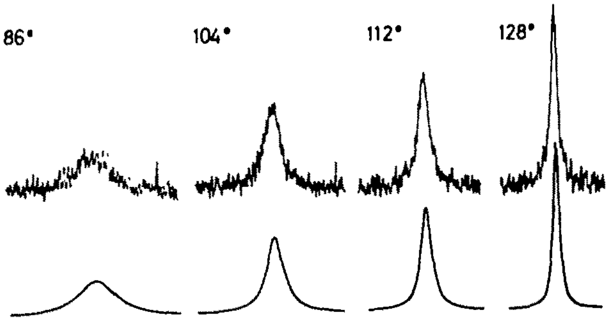


Fig 3. Observed and calculated ^{13}C-NMR spectra of bullvalene in the fast exchange region.

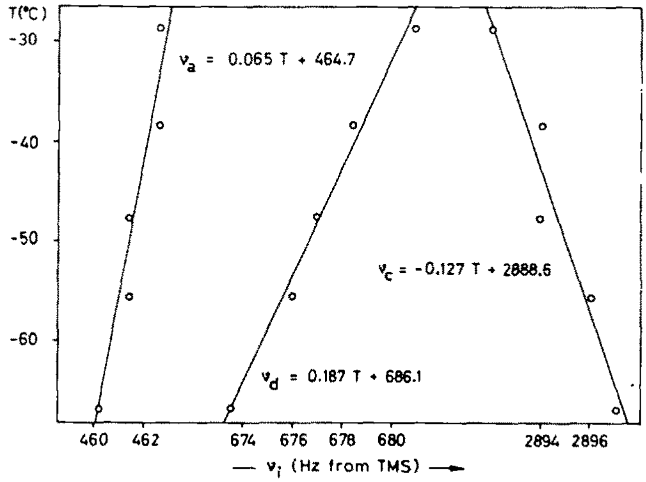


Fig 4. Observed temperature dependence of the Larmorfrequencies of C_a, C_c, and C_d. The equations are the result of a least squares fit of the data.

was assumed. $\delta(C_b)$ was found to be temperature independent.

Six measurements between −59 and 0°C were then used for the lineshape analysis. In order to reproduce the experimental spectra satisfactorily it was necessary to introduce populations of p_a = 2·42, p_b = 3·01, p_c = 3·00, and p_d = 0·93 that differ in the case of C_a and C_d significantly from the statistical ratio 3:3:3:1. No systematic variations of these "mole fractions" with temperature could be detected. For spectra showing only slight exchange broadening it was also evident that the consideration of a uniform natural linewidth did not allow a good reproduction of the lineshape. Individual linewidth parameters were used therefore, but the differences amounted to less than 20%. At higher temperatures this point was found to be less important and the linewidth of the tetramethylsilane ^{13}C resonance was employed as natural linewidth for all sites.

In the fast exchange region six spectra were recorded between 86 and 128°C. The calculations were based on theoretical population ratio of 3:3:3:1 since the lineshape proved to be independent of fairly large variations of these parameters. Furthermore, the ratio determined for the apparent populations at −67°C is not expected to hold also at higher temperature.

Rate constants and activation parameters are collected in Tables 1 and 2, respectively. The Arrhenius plot of the data is given in Fig 5; ΔH‡ and ΔS‡ were obtained from a log (k/T) − 1/T plot.[1]

Finally, in order to investigate a possible influence of various experimental parameters on the results, spectra were recorded at different settings for pulse width, sampling rate, delay time, the power of the ^1H-decoupling field H_2 and the time constant used for the exponential multiplication of the data. In each case a complete lineshape calculation was performed to determine the k-value. As Table 3 demonstrates, no such influence was detected.

Table 1. Rate constants for the degenerate cope rearrangement of bullvalene

T(°C)	k(sec^{-1})
−59·3	0·6
−37·3	20·0
−28·7	33·0
−19·1	95·0
−10·2	220·0
0	670·0
86	340,000·0
93	520,000·0
104	800,000·0
112	1300,000·0
120	1900,000·0
128	2800,000·0

DISCUSSION

The results obtained in this study give no indication of systematic errors present in ^{13}C-NMR lineshape analysis. In particular the good agreement between the activation parameters obtained by separate treatment of the data from the spectra below and above the coalescence temperature seems to indicate that the use of fictitious populations, at least to the extent necessary in the present case, does not introduce serious errors. Even the neglect of the temperature dependence of the resonance frequencies that caused a change of the total spectral range of 30 Hz for the fast exchange region, was not sufficient to affect the results in a significant way, as the respective numbers in Table 2 demonstrate.

From the variations of the experimental settings investigated in Table 3 the mathematical filtering by exponential multiplication seems, at first hand, the

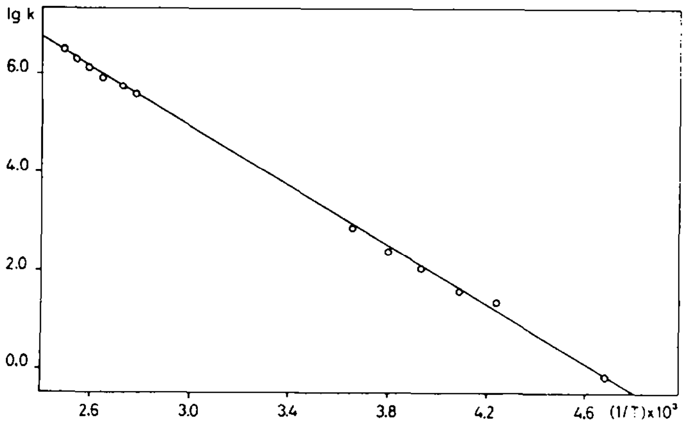


Fig 5. Arrhenius plot of the rate constants obtained for the degenerate Cope rearrangement of bullvalene.

Table 2. Activation parameters of the degenerate cope rearrangement of bullvalene as obtained by dynamic NMR spectroscopy

Nucleus	Solvent	Temp (°C)	E_a[a]	log A	$\Delta H^{\ddagger c,a}$	$\Delta S^{\ddagger c,b}$	Reference
^{13}C [a]	$C_2H_2Cl_4$	−59–0	13·4 ± 0·6	13·5 ± 0·5	12·9 ± 0·6	1·7 ± 2·4	this work
^{13}C [a]	$C_2H_2Cl_4$	86–128	14·2 ± 0·4	14·2 ± 0·3	13·5 ± 0·4	3·9 ± 1·1	this work
^{13}C [a]	$C_2H_2Cl_4$	−59–128	13·9 ± 0·1	14·0 ± 0·1	13·3 ± 0·1	3·4 ± 0·4	this work
^{13}C [a][c]	$C_2H_2Cl_4$	86–128	13·8 ± 0·9	13·9 ± 0·5	13·0 ± 0·9	2·8 ± 2·4	this work
^{1}H [a]	—	10·5–82·7	11·8 ± 1·0	12·3	—	—	13
^{1}H [a]	—	—	11·7 ± 0·2	—	—	—	14
^{1}H [b]	C_2Cl_4	25–123	12·8 ± 0·1	12·9	—	—	15

[a] Lineshape analysis; [b] Spin echo method.

[a] In kcal/mole.

[b] In entropy units.

[c] Calculations done with neglect of temp dependent chemical shifts.

Table 3. The influence of experimental parameters[3,17] on the rate constant of the degenerate cope rearrangement of bullvalene

Temp (°C)	Experimental parameter varied		Rate constant k (sec^{-1})
−23·0	dwell time[a]	100 μsec	59
		125 μsec	59
		166 μsec	59
−26·3	delay time	40 μsec	46
		70 μsec	46
		100 μsec	53
−23·4	pulse width	6 μsec	55
		10 μsec	55
		14 μsec	55
		18 μsec	55
−25·4	decoupler power[b]	82	44
		60	49
		37	48
−22·4	exponential factor[c]	0·0	70
		−2·5	68
		−5·0	70

[a] Reciprocal acquisition rate (data points per sec).

[b] In % of full power.

[c] TC in $x'_j = x_j \exp[j(TC)/N]$ j = 0, 1, 2, ... N.

most dangerous, since this artificial data manipulation yields a better signal to noise ratio but increases the linewidth. As the results show, however, to the extent used here, where linewidth of the order of 25 Hz were recorded, no effect is seen in the rate constants. Furthermore the reference line used to determine the natural linewidth is affected in the same manner and this corrects for any artificial linebroadening in an empirical fashion.

Compared to the ^{1}H-NMR results that are given in Table 3 our ^{13}C-NMR results seem to yield a somewhat higher energy barrier for the valence isomerization of **1**. However, the natural linewidth and the spin–spin coupling were neglected in the calculations of the ^{1}H-NMR lineshape,[13] as was the chemical shift difference for the olefinic protons H_b and H_c. Because of the large exchange broadening observed for **1** these assumptions did not seem serious. They might, however, add up to systematic error. Additional linebroadening caused by these effects renders the rate constants above coalescence too small and below coalescence too large. Accordingly, E_a and the frequency factor will be found too small. Furthermore, the temperature range used for the measurement was smaller than that in the present investigation. This is also true for the spin echo work,[15] the results of which come closest to our data. In fact these two data sets agree quite well, if a realistic estimate of the errors in the activation parameters of *ca* 0·5–1·0 kcal/mole for the energy is made. The entropy of the valence isomerization is expected to be small and positive (R ln 3 or 2·2 e.u. from a consideration of symmetry numbers), in agreement with our findings. To our knowledge, no details about the measurements by Oth *et al.*[14] have appeared so far.

It is interesting to note that a comparative dynamic ^{13}C-NMR study has also been performed for h^5,h^1-dicycloheptadienyl dicarbonyliron.[18] Similar to our results the activation parameters obtained from ^{13}C-NMR were found to be higher than those determined earlier by proton NMR. This was explained by the use of apparently incorrect natural line width, the neglect of spin coupling, as well as the smaller temperature range used for the ^{1}H-NMR measurements.

The present investigation also clearly indicates the possible drawbacks of dynamic ^{13}C-NMR spectroscopy mentioned already by Gansow *et al.*[11]: From the whole temperature range studied a sizable fraction of 80°C had to be omitted (*cf* Fig 5) since the lines were too broad to achieve sufficient signal to noise ratio in a reasonable time, especially when the accumulation period is limited by the condition of constant temperature. Much valuable information is thus sacrificed from the region around the coalescence point, where the lineshape is most sensitive to the dynamic process. As in other branches of NMR spectroscopy, ^{13}C-NMR will, therefore, widen the applications of the technique but by no means substitute ^{1}H-NMR.

EXPERIMENTAL

Compound **1** was synthesized according to Schröder,[19] recrystallized from EtOH and sublimed several times. ^{13}C-NMR measurements were performed with a Bruker HX-90 spectrometer operating at 22·628 MHz and equipped with ^{2}H-stabilization, ^{1}H broadband decoupler, and a 12 K Nicolet-1083 computer. Spectral range for the measurements was 5000 Hz, the experimental settings were kept constant for a series of measurements at different temperatures; 3000–6000 transients were accumulated.

The Bruker temp unit BS-100/700 was used to control the probe temp during each measurement. Below 0°C the temp was measured before and after each spectrum was recorded by the introduction of a thermocouple into a nonspinning sample tube that contained the relevant solvent. At high temps a calibrated thermometer was used for this purpose. The temp readings for each data point did not differ by more than 1°C. 10 mm sample tubes were used with a 0·242 molar soln of **1** in a mixture of $CHCl_2CHCl_2/CDCl_3/TMS$ (84:13:3) for low temp work. In the fast exchange region a 0·41 molar soln of **1** in $CHCl_2CHCl_2/DMSO\text{-}d_6$ (91:9) with the solvent peak as reference line was used.

The measurements at different experimental conditions (*cf* Table 3) were made on a 0·81 molar soln of **1** in $CDCl_3$ with *ca* 5% TMS as internal reference. In order to account for the temp dependence of the δ-values of **1** in this solvent 5 measurements between −74 and −54°C were performed.

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Note added in proof: Preliminary results of a dynamic ^{13}C-NMR study of **1** have recently been reported by H. Nakanishi and O. Yamamoto, *Tetrahedron Letters* 1803 (1974).

LITERATURE

[1] For a review see G. Binsch, *Topics in Stereochemistry* 3, 97 (1968)

[2] R. R. Ernst and W. A. Anderson, *Rev. Sci. Instrum.* 37, 93 (1966)

[3] T. C. Farrar and E. D. Becker, *Pulse and Fourier Transform NMR*, Academic Press, New York (1971)

[4] H. Günther, *NMR-Spektroskopie*. G. Thieme Verlag, Stuttgart (1973)

[5] R. R. Ernst, *Plenary Lecture, XIth European Congress on Molecular Spectroscopy*. Tallinn, USSR (1973)

[6] A. Allerhand, H. S. Gutowsky, J. Jonas, and R. A. Meinzer, *J. Am. Chem. Soc.* **88**, 3185 (1966)

[7] K. F. Kuhlmann and D. M. Grant, *Ibid.* **90**, 7355 (1968)

[8] F. C. Farrar, S. J. Druck, R. R. Shoup, and E. D. Becker, *Ibid* **94**, 699 (1972)

[9] D. K. Dalling, D. M. Grant, and L. F. Johnson, *Ibid* **93**, 3678 (1971)

[10] H. J. Schneider, R. Price, and T. Keller, *Angew. Chem.* **83**, 759 (1971)

[11] O. A. Gansow, J. Killough, and A. R. Burke, *J. Am. Chem. Soc.* **93**, 4297 (1971)

[12] G. Schröder, *Angew. Chem.* **75**, 722 (1963); W. v. E. Doering and W. R. Roth, *Tetrahedron* **18**, 67 (1962)

[13] M. Saunders, *Tetrahedron Letters* 1699 (1963)

[14] J. M. Gilles and J. F. M. Oth, unpublished, cited by G. Schröder, J. F. M. Oth, and R. Merenyi, *Angew. Chem.* **77**, 774 (1965)

[15] A. Allerhand and H. S. Gutowsky, *J. Am. Chem. Soc.* **87**, 4092 (1965)

[16a] P. W. Anderson, *J. Phys. Soc. Japan* **9**, 316 (1954); [b] R. Kubo, *Ibid.* **9**, 935 (1954); [c] R. A. Sack, *Mol. Phys.* **1**, 163 (1958)

[17] D. Ziessow, *On-line Rechner in der Chemie*. Walter de Gruyter, Berlin (1973)

[18] D. J. Ciappenelli, F. A. Cotton, and L. Kruczynski, *J. Organo-metallic Chem.* **42**, 159 (1972)

[19] G. Schröder, *Chem. Ber.* **97**, 3140 (1964)