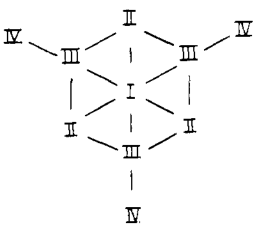
Scheme I



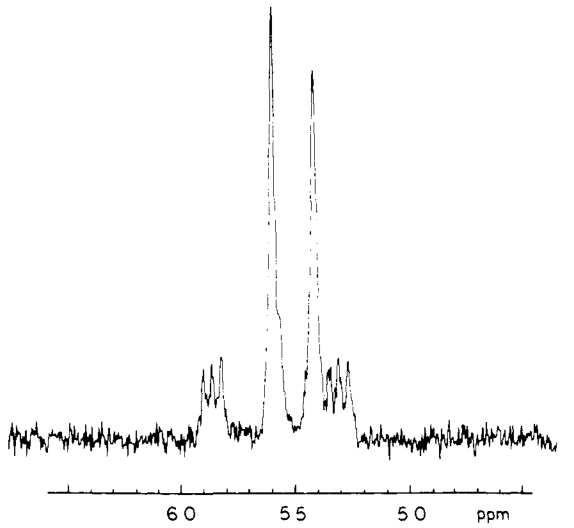


Figure 1. ^{13}C NMR spectrum of the monodeuterated ion.

methylene hydrogens) moves upfield (δ between them = 0.357 at −135 °C). However, a peak of area 2 is also seen closer to the original position but shifted *downfield* ($\delta \sim 0.04$ at −135 °C).

These results indicate that the isotope effects for deuterium in the nonequivalent positions have *opposite signs*. Conclusive confirmation comes from the ^{13}C NMR spectrum of the monodeuterated ion (Figure 1) which shows clearly this remarkable and unanticipated change in the sign of the equilibrium isotope effect. These shifts vary with temperature in the expected fashion for *equilibrium isotope effects*.

Observing *equilibrium* isotope effects indicates that the tricyclobutonium ion I is *not* the main species present. We must therefore consider a degenerate set of rapidly equilibrating ions of lower symmetry (II, III, and IV). The opposite signs of the isotope effects and the large difference in Δ imply that the *differences* both of the chemical shift and of the force constants between the two types of rapidly equilibrating hydrogens are *extremely* different. We would not expect this for either bent cyclobutyl IV or cyclopropylcarbinyl cation II, although delocalization might produce moderate differences. However, the bicyclobutonium ion III has one pentacoordinated carbon which might have two extremely different CH bonds. Pentacoordinated carbons and the attached hydrogens often have very unusual chemical shifts. It might be anticipated that the vibration frequencies of CH groups attached in different positions could also differ considerably. The striking difference in Δ and the equilibrium isotope effects of opposite sign may be due to a large difference in the bonding and, hence, the frequencies and force constants of the two hydrogens on the pentacoordinated carbon of III.

If III is the main species present, the rapid degenerate equilibrium might occur via I, or II, which could represent transition states with the barrier less than ~3 kcal. Bent cyclobutyl cation IV has the same symmetry as bicyclobutonium ion but might be distinguished from it by considering whether bending brings the diagonally related carbons within bonding distance or not.

Roberts and Olah[3] interpreted a small temperature dependence of the ^{13}C NMR spectrum of this ion as indicating a minor species in rapid equilibrium with the major ion. We observed a splitting of 0.4 ppm at −96 °C between the methine peaks of the two isomeric monodeuterated cations which offers strong support to this idea. The minor isomer might correspond to II or, less likely, to a structure similar to I or IV.

Acknowledgment. We acknowledge support of this research by a grant from the National Science Foundation and by a fellowship to H.U.S. by the Deutsche Forschungsgemeinschaft. All NMR spectra were obtained on the HX-270 spectrometer of the Southern New England High Field NMR Facility supported by the BBR office of the NIH.

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Received May 20, 1980

Cyclization Dynamics of Polymers. 2. Dynamics and Thermodynamics of End-to-End Cyclization of Polystyrene in a Θ Solvent

Sir:

Since the early part of this century, chemists have been fascinated by the cyclization of flexible chain molecules. The discovery of macrocyclic principles in musk extracts in the 1920's prompted intense interest in the synthesis of medium-sized rings.[1] This interest continues today, spurred by the importance of macrolide antibiotics. In 1934, Kuhn related the cyclization probability, $W(0)$, of a polymer to its other conformational properties.[2] Since then, polymer chemists (most notably Semlyen[3]) have examined ring chain polymerization in detail, comparing measured cyclization equilibrium constants with values calculated from models developed by Jacobsen and Stockmayer[4] and Flory and Semlyen.[5]

A new chapter in this history was opened by Wilemski and Fixman,[6] who examined theoretical models of the *dynamics* of end-to-end cyclization in polymers. These authors related the rate constant for end-to-end cyclization, $k_{\rm cy}$, to the various relaxation times of both the Rouse–Zimm ball-and-spring model and also the harmonic spring model of long polymer chains. Their work and subsequent papers by Doi[7] emphasize that $k_{\rm cy}$ is related to the slowest normal mode of the polymer. Since this mode is important in other hydrodynamic interaction sensitive properties of polymers, Perico and Cuniberti[8] were able to use intrinsic viscosity data to parameterize the Wilemski–Fixman formalism and predict values for $k_{\rm cy}$.

These theoretical papers[6-9] have had an important impact on the field of polymer dynamics. Since the formulations involved simplifying assumptions at various stages in the development of the models, further refinements will depend upon experiments which can provide quantitative assessment of the theories. There are many experimental questions which need to be asked. Among them are the following: (1) What are the magnitudes of $k_{\rm cy}$? (2) What is its chain length dependence? (3) Is there a relationship between $k_{\rm cy}$ and $K_{\rm cy}$, the equilibrium constant for end-to-end cyclization?

Intramolecular excimer formation between chromophores attached to the ends of a polymer chain provides a tool for answering

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(1) For a review, see G. M. Bennett, *Trans. Faraday Soc.*, **37**, 794 (1941).

(2) W. Kuhn, *Kolloid-Z.*, **68**, 2 (1934).

(3) J. A. Semlyen, *Adv. Polym. Sci.*, **21**, 41 (1976).

(4) H. Jacobsen and W. H. Stockmayer, *J. Chem. Phys.*, **18**, 1600 (1950).

(5) P. J. Flory and J. A. Semlyen, *J. Am. Chem. Soc.*, **88**, 3209 (1966).

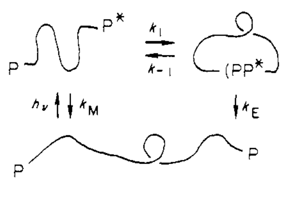
(6) (a) G. Wilemski and M. Fixman, *J. Chem. Phys.*, **58**, 4009 (1973); *ibid.*, **60**, 866, 878 (1974); (b) M. Fixman, *ibid.*, **69**, 1527, 1538 (1978).

(7) (a) M. Doi., *Chem. Phys.*, **9**, 455 (1975); *ibid.*, **11**, 107, 115 (1975); (b) S. Sanagawa and M. Doi, *Polym. J.*, **7**, 604 (1975); *ibid.*, **8**, 239 (1976); (c) M. Sakata and M. Doi, *ibid.*, **8**, 409 (1976).

(8) (a) A. Perico and C. Cuniberti, *J. Polym. Sci., Polym. Phys. Ed.*, **15**, 1435 (1977); (b) A. Perico, P. Piaggio, and C. Cuniberti, *J. Chem. Phys.*, **62**, 4911 (1975).

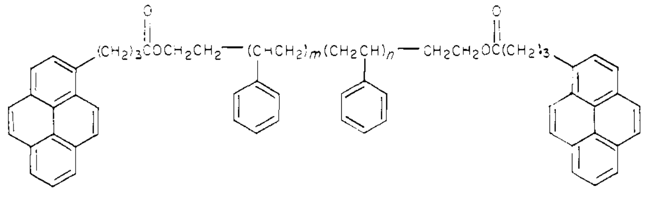
(9) M. G. Brereton and A. Rusli, *Polymer*, **17**, 395 (1976).

Scheme I



all of these questions.[10,11] According to the kinetic scheme below (Scheme I), excimer formation can be described by a first-order rate constant, $\langle k_1 \rangle$ (averaged over the molecular weight distribution of the sample);[11b] k_E and k_M describe, respectively, the sums of emissive and radiationless decays of the excimer and the locally excited chromophore (the "monomer" decay), and k_{-1} describes the dissociation of the excimer to the open, locally excited state.

Using the techniques of anionic polymerization, we have synthesized HO-terminated polystyrene of molecular weights $\bar{M}_n$ = 3000–100000 with polydispersities $\bar{M}_w/\bar{M}_n$ = 1.2–1.7. These were further fractionated by silica gel chromatography to give polymers of narrow polydispersity ($\bar{M}_w/\bar{M}_n$ = 1.03–1.13) and esterified with the acid chloride of pyrenebutyric acid. The polymers for photochemical studies were ultimately purified by gel permeation chromatography to remove traces of fluorescent low molecular weight materials. This material has the following structure.



$m \approx n$

Fluorescence decay measurements were carried out on rigorously degassed dilute solutions of the polymer in cyclohexane at 34.5 °C, the Θ temperature. Decay profiles were independent of concentration in the domain of 7×10^{-7} to 5×10^{-6} M. The methyl ester (**1**) of 1-pyrenebutyric acid was chosen as a model compound. It decayed exponentially over 7 lifetimes. The mechanism in Scheme I predicts for decay of monomer $I_M(t)$ and excimer $I_E(t)$ emission the relations seen in eq 1 and 2. Rate

$$I_M(t) = a_1 \exp(-\lambda_1 t) + a_2 \exp(-\lambda_2 t) \qquad (1)$$

$$I_E(t) = a_3 [\exp(-\lambda_2 t) - \exp(-\lambda_1 t)] \qquad (2)$$

constants are a complicated function of the decay constants. Following Birks,[12] we define $X = k_M + \langle k_1 \rangle$ and $Y = k_E + k_{-1}$. Rate constants are obtained from the values of a_1/a_2 in conjunction with the expression given in eq 3 and the lifetime τ_M of the model compound **1** ($\tau_M = k_M^{-1}$).

$$\lambda_1, \lambda_2 = \frac{1}{2}[(X + Y) \mp \{(Y - X)^2 - 4\langle k_1 \rangle k_{-1}\}^{1/2}] \qquad (3)$$

These expressions represent testable hypotheses: When the chains are very long so that $4\langle k_1 \rangle k_{-1} \ll (Y - X)^2$, the decay of the locally excited state should be exponential. While polydisperse materials show pronounced deviations from exponential decays, long-chain samples ($\bar{M}_n > 10^4$), properly fractionated ($M_w/M_n \leq 1.1$), give decay curves that can be fit to the exponential function over more than 6 lifetimes. Under these circumstances, $\lambda = X$, and $\langle k_1 \rangle$ can be obtained from the expression[13] given in eq 4.

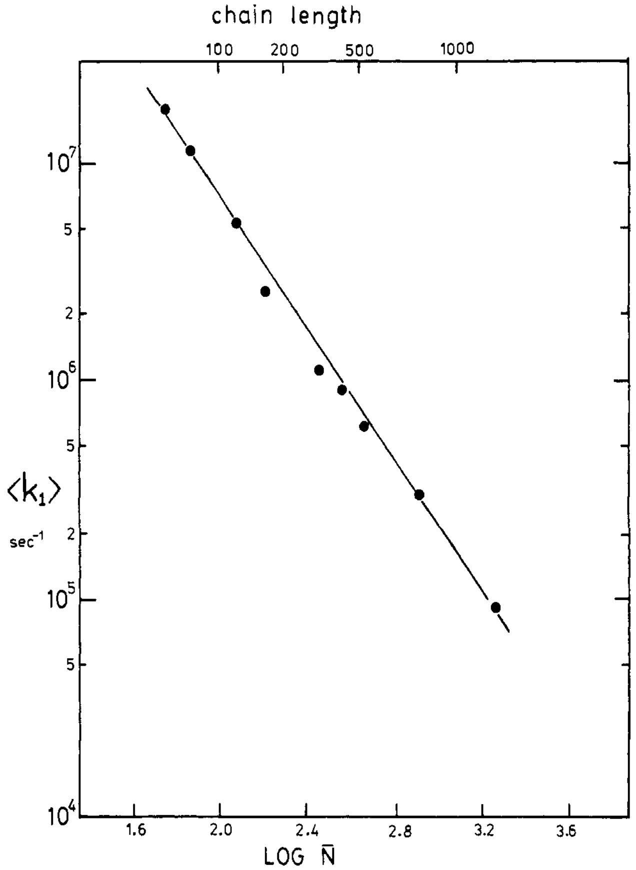


Figure 1. The mean rate constant for end-to-end cyclization, $\langle k_1 \rangle$, in polystyrene as a function of mean chain length, $\bar{N}$, in cyclohexane at 34.5 °C, the Θ point. Solutions were 2×10^{-6} M in polymer.

$$\langle k_1 \rangle = \lambda - k_M \qquad (4)$$

For shorter chains, deviations from exponential behavior for $I_M(t)$ are observed. As predicted by eq 1 and 2, monomer and excimer intensity curves give values of λ_1 and of λ_2 which are identical within experimental error. Indeed, in all of our samples, λ_2^{-1} is approximately equal to 40 ns.

Values of $\langle k_1 \rangle$ calculated from our data are plotted against chain length [N] in Figure 1. From these data, it is clear that log $\langle k_1 \rangle$ is a strong and linear function of log N. Thus, the rate constant for end-to-end cyclization is of the form given in eq 5.

$$k_{cy} = AM^{-\gamma} \qquad (5)$$

Since k_1 and $\bar{M}_n$ represent different averages over the molecular weight distribution in each polymer sample, values of A and γ were obtained by reaveraging the molecular weights of each polymer over the known distribution for each sample.[11]

Theoretical treatments of k_{cy} predict behavior of the form of eq 5 for flexible polymers in a Θ solvent.[6-9] For both the harmonic spring model[6,7] and the nondraining Rouse chain, the critical exponent is predicted to have the value $^3/_2$. Our experimental value[14] of γ = 1.62 ± 0.10 is in good agreement with these predictions.

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(10) C. Cuniberti and A. Perico, *Eur. Polym. J.*, **13**, 369 (1977).

(11) (a) M. A. Winnik, A. E. C. Redpath, and D. H. Richards, *Macromolecules*, **13**, 328 (1980). (b) We use the term k_{cy} to describe the theoretical dynamically controlled rate constant for end-to-end cyclization. It refers to chains of unique length. We use $\langle k_1 \rangle$ to describe the rate constant for intramolecular excimer formation between the chain ends extracted from experimental data. It refers to a particular molecular weight distribution in the polymer sample. Since excimer formation is diffusion controlled, for chains of discrete length, $k_1 = k_{cy}$.

(12) J. B. Birks, "Photophysics of Aromatic Molecules", Wiley, New York, 1970, Chapter 7.

(13) For molecular weights greater than 20000, λ and k are of comparable magnitude, and the precision of k_m values is poor. Relative values of $\langle k_l \rangle$ can be obtained from the intensity ratio of monomer to excimer fluorescence 11a: $(I_e/I_m)_1/(I_e/I_m)_2 = \langle k_1 \rangle_1/\langle k_1 \rangle_2$, even when the excimer fluorescence is very weak.

(14) The uncertainty in γ has two sources. One is statistical and arises from the measurements. The second is the uncertainty in absolute values of $\bar{M}_n$ and $\bar{M}_w$ determined by gel permeation chromatography by using as standards polystyrene samples from Pressure Chemicals Co. A third factor influencing γ is the effect of the short spacer chains separating the pyrenes from the polymer. The perturbation caused by structural features of the spacer is unknown, but its net effect would be greater on the lower molecular weight polymers.

When nonexponential decays were observed for pyrene fluorescence, we could calculate all four rate constants in Scheme I. This made it possible for us to obtain the equilibrium constant for end-to-end cyclization [$\langle K_1 \rangle = \langle k_1 \rangle / k_{-1}$] and ask the important question of whether k_{cy} and K_{cy} have the same dependence upon chain length. Our data indicate that $k_{-1} = (2.7 \pm 0.5) \times 10^6\ \mathrm{s}^{-1}$ at 34.5 °C in cyclohexane for our five lowest molecular weight samples. Since k_{-1} is independent of chain length, K_{cy} must also vary with $M^{-1.62\pm0.1}$.

There are two features of this result which should be noted. The first is that polymer chains in Θ solvents are thought to have a Gaussian distribution of end-to-end distances.[15,16] For such a chain, the cyclization probability and thus K_{cy} should vary as $M^{-3/2}$. As in the case of polysiloxanes,[3] this prediction is (within experimental error) verified. The second aspect which we would like to point out is that there is currently some controversy about whether dynamic and thermodynamic behavior of polymers scale according to the same critical exponents.[17] The key aspects of the problem concern the behavior of polymer chains in good solvents, and not in Θ solvents. Our results provide an example in which dynamics and thermodynamics of end-to-end cyclization appear to have the same dependence on chain length in a Θ solvent, and they open the door to similar experiments in solvents where the excluded volume effects on the chains are substantial.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We also thank NSERC-Canada for its financial assistance.

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(16) M. Nierlich, J. P. Cotton, and B. Farnoux, *J. Chem. Phys.*, **69**, 1 (1978).

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Received May 19, 1980

Electronic Excited-State Analysis by Magnetic Circular Dichroism of d^6 (Alkylamino)pentacarbonyl Complexes, $[M(CO)_5A]^0$ (M = Cr, Mo, W)

Sir:

Transition-metal carbonyls are a class of photochemically and photocatalytically fascinating molecules undergoing diverse excited-state reactions, often with high quantum yields. Yet, the identity of the excited state for light absorption is nearly never directly identified. We report here direct band identifications for several Cr, Mo, and W molecules, $[M(CO)_5A]$ (Cr, piperidine, cyclohexylamine; Mo, cyclohexylamine; W, ammonia piperidine, cyclohexylamine), by using magnetic circular dichroism (MCD) spectroscopy as follows.[1,2]

The definitive assignments come from MCD analysis applied to these closed-shell molecules and concern the (i) identification of ^1E excited states and their differentiation from excitations to C_{4v} states $^1A_1$, $^1A_2$, $^1B_1$, and $^1B_2$, viz., MCD *A* terms can occur only for $^1A_1 \rightarrow {}^1E$, and (ii) the *sign* of the *A* term, since it can reveal the *orbital* fate of the excitation.

Specifically here, we consider the optical bands of $M(CO)_5A$ which are to lower energy of the red-most band of $M(CO)_6$ as d–d transitions,[3] since $Dq(\text{amine}) < Dq(\text{CO})$. For example, at least bands I (~430 nm), II (~400 nm), and II′ (~380 nm, shoulder) of $W(CO)_5A$ (Figure 1) are of d–d type,[3] since $W(CO)_6$ has its two lowest energy bands at ~350 and ~310 nm (Figure 1). Furthermore, for interpretation of the d–d transitions of $M(CO)_5A$, the photoelectron spectroscopy (PES) data[4] for amines are of interest here, since they established that the t_{2g} HOMO of the ground state is split into energy order e^4 ($\sim d_{xz}, d_{yz}$) > $b_{2g}{}^2$ ($\sim d_{xy}$). Next, the decision about how to associate the excited-state MOs, a_1 ($\sim d_{z^2}$ M) or b_1 ($\sim d_{x^2-y^2}$ M), with a d–d excitation $^1A_1 \rightarrow {}^1E$ [from e^4 ($\sim d_{xz}, d_{yz}$ M) → $e^3 a_1{}^1$ ($\sim d_{z^2}$ M) or e^4 ($\sim d_{xz}, d_{yz}$ M) → $e^3 b_1{}^1$ ($\sim d_{x^2-y^2}$ M)] can be made directly through MCD, since *A*/*D* ratios have opposite signs for the configuration changes, which will be shown subsequently.

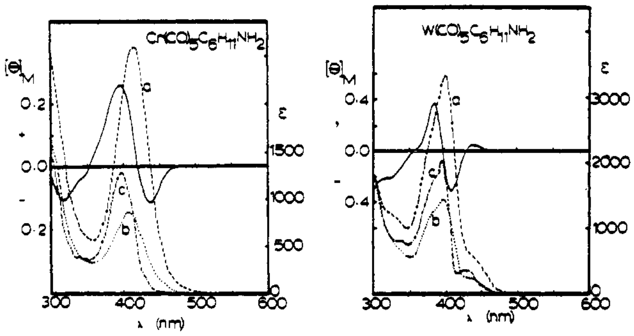
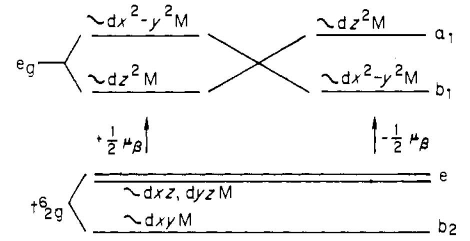


Figure 1. Optical and magnetic circular dichroism spectra of $M(CO)_5$ (cyclohexylamine): (a) MCD and optical spectra in dichloromethane at 300 K, (b) in EPA at 300 K, and (c) in EPA at 77 K (uncorrected for volume contractions). The solid line spectrum is the MCD of $[M(CO)_5A]$. $[\theta]_M$ is the molar ellipticity per gauss.



D is the electric dipole strength for the transition from the ground state (state function *a*) to the excited state (state function *j*), i.e., $D(a \rightarrow j)$ equals $1/d_a \sum_{a,j} |\langle a|m|j\rangle|^2$, or $|\langle {}^1A_1||m||{}^1E\rangle|^2$, *m* is the electric dipole operator ($m_x + m_y$), *a* is $^1A_1$, and *j* is ^1E, and $\langle {}^1A_1||m||{}^1E\rangle$ is basis free.[5] Also, with *a* and *j* in the complex basis and μ and *m* real, the MCD *A* term equals $^1/_2 \sum \langle j|\mu|j\rangle \cdot Im\langle a|m|j\rangle \times \langle j|m|a\rangle$, or $-2^{-3/2} i \langle E||\mu||E\rangle |\langle A_1||m||E\rangle|^2$, so that *A*/*D* equals $-2^{-3/2} i \langle {}^1E||\mu||{}^1E\rangle$, where $\langle {}^1E||\mu||{}^1E\rangle$ is a basis-free magnetic dipole state integral[2,5] which we evaluate ($\mu_z = \beta L_z$) as in eq 1.

$$\langle {}^1E||\mu||{}^1E\rangle = (\beta) 2^{1/2} \langle {}^1E_x|L_z|{}^1E_y\rangle \tag{1}$$

Evaluation[6] of $\langle L\rangle$ for four electrons of $^1E[e^3$ ($\sim d_{xz}, d_{yz}$ Cr) $a_1{}^1$ ($\sim d_{z^2}$)] or $^1E[e^3\ b_1{}^1$ ($\sim d_{x^2-y^2}$)] simplifies to the one-electron integrals, as already shown (eq 2 and 3).[7] Furthermore, we will

$$\langle {}^1E\ e^3\ a_1{}^1(z^2)||L||{}^1E\ e^3\ a_1{}^1(z^2)\rangle = \langle e||l||e\rangle \tag{2}$$

$$\langle {}^1E\ e^3\ b_1{}^1(x^2-y^2)||L||{}^1E\ e^3\ b_1{}^1(x^2-y^2)\rangle = -\langle e||l||e\rangle \tag{3}$$

be selecting the *z* component, l_z, for purposes of evaluating $\langle e||l||e\rangle$ as $-2^{1/2}\langle e_x|l_z|e_y\rangle$. Dominant contributions to MOs with transformation behavior of e_x, e_y will be assumed to come from d_{yz}, d_{xz} orbitals of the metal,[6] on which operator l_z is based, so $\langle e_x|l_z|e_y\rangle$

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(1) A. F. Schreiner, S. Amer, W. M. Duncan, R. M. Dahlgren, and J. Zink, presentation at the 178th National Meeting of the American Chemical Society, Washington, D.C., Sept 1979; Abstr. 219, Inorganic Chemistry. This constitutes the first MCD report of molecules $[M(CO)_5A]$.

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(7) R. M. E. Vlick and P. J. Zandstra, *Chem. Phys. Lett.*, **31**, 487 (1975).

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