Theoretical Studies of Trimethylene[1]

Albert K. Q. Siu, Willard M. St. John, 3rd, and Edward F. Hayes*

Contribution from the Department of Chemistry, Rice University, Houston, Texas 77001. Received March 12, 1970

Abstract: Nonempirical self-consistent-field molecular orbital theory, plus configuration interaction, is used to investigate the open forms of cyclopropane. These calculations indicate the presence of a stable minimum corresponding to an open form which has the terminal methylene groups lying in the C–C–C plane (0,0 form). The singlet and triplet states for this 0,0 open form are found to have about the same energy. For this 0,0 open form the rotational barrier for nonconcerted rotation of the terminal methylene is found to have a number of novel features which distinguishes it from other rotational barriers such as ethane, which have been studied previously by nonempirical methods. The presence of a stable minimum corresponding to an open form with the terminal methylene perpendicular to the C–C–C plane is suggested by the LCAO–MO–SCF results. The existence of such a minimum is not supported by the configuration-interaction calculations.

Recent studies of the pyrolysis of cyclopropanes[2] and pyrazolines[3] suggest that the intermediates involved in these two reactions may not be the same. Hoffmann[4] has proposed the existence of a planar trimethylene intermediate to explain the crossover stereochemistry of cyclopropane formation from pyrazolines. However, Berson and Balquist's[2a] study of the pyrolysis of tetramethylcyclopropane-d_6 and Bergman and Carter's[2b,c] study of the pyrolysis of 1-ethyl-2-methylcyclopropane suggest that Hoffmann's trimethylene intermediate may not be involved in the pyrolysis of cyclopropanes. In view of the current interest in the detailed mechanism of these reactions, it seems worthwhile to see what insight can be gained from quantum-mechanical studies of the cleavage of the carbon–carbon bond in cyclopropane.

There are only two previous theoretical studies of carbon–carbon bond cleavage in cyclopropane. In one of these[4] the extended Hückel method was used. These calculations indicate the existence of a trimethylene intermediate with a C–C–C bond angle of about 125° with trigonal terminal methylene groups coplanar with the carbon skeleton. In the present paper, the nonempirical self-consistent-field (SCF) molecular orbital (MO) theory,[5a] plus configuration interaction (CI),[5b] is used to investigate some important features of the potential energy surface for carbon–carbon bond cleavage in cyclopropane. Previously, Buenker and Peyerimhoff[6] used similar methods to study cyclopropane. However, they did not investigate the rotation of the terminal methylene groups.

Recently both Berson and Balquist[2a] and Bergman and Carter[2b] have discussed the possible existence of a trimethylene diradical. The bond rotations in the trimethylene diradical are thought to be fast relative to recrystallization. Apparently, there is no direct experimental evidence for either the existence of a trimethylene diradical or a planar trimethylene. For this reason, information about the electronic structure, C–C–C bond angle, and barriers to internal rotation for the trimethylene diradical and planar trimethylene may be particularly useful.

The results reported in this paper were obtained using the MOLE Quantum Chemistry System.[7] This is a general purpose program for quantum-mechanical calculation of the electronic structure and electronic energy of molecules.

Basis Orbitals

The basis sets for these calculations are grouped Gaussian orbitals. For carbon the s-type orbitals are the 1s, 2s, and 3s grouped orbitals reported by Whitten.[8] The 2p orbitals are not constructed from Gaussian-lobe functions. Instead, Cartesian Gaussians are used. These were obtained from Huzinaga's 9,5 basis-set calculations on the first-row atoms.[9] The 1s grouped orbital for hydrogen is the five-term 1s obital reported by Whitten only scaled by a factor of 1.414, as suggested by Fink, Whitten, and Allen.[10] These basis sets are about double-ζ accuracy for the atomic calculations. This is the same accuracy as the basis orbitals used in many previous studies of ABC-type molecules.[11]

Geometrical Considerations

The number of degrees of freedom in the $C^{(1)}H_2$–$C^{(2)}H_2$–$C^{(3)}H_2$ potential surface was reduced by fixing the $C^{(1)}$–$C^{(2)}$ and $C^{(2)}$–$C^{(3)}$ bond distances at 2.76 bohrs and the C–H distances at 2.06 bohrs. The H–C–H angles were taken to be 115°. The remaining degrees of freedom are the $C^{(1)}$–$C^{(2)}$–$C^{(3)}$ bond angle and the rotations of the terminal methylene groups out

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* Address correspondence to this author.

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[2] (a) J. A. Berson and J. M. Balquist, *J. Amer. Chem. Soc.*, **90**, 7343 (1968); (b) W. L. Carter and R. G. Bergman, *ibid.*, **90**, 7344 (1968); (c) R. G. Bergman and W. L. Carter, *ibid.*, **91**, 7411 (1969).

[3] R. J. Crawford and A. Mishra, *ibid.*, **87**, 3768 (1965); **88**, 3963 (1966); D. E. McGreer, N. W. K. Chiu, M. G. Vinje, and K. C. K. Wong, *Can. J. Chem.*, **43**, 1407 (1965).

[4] R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968).

[5] (a) C. C. J. Roothaan, *Rev. Mod. Phys.*, **32**, 1791 (1960); **23**, 69 (1951); (b) for general information about configuration interaction, see, for instance, R. G. Parr, "Quantum Theory of Molecular Electronic Structure," W. A. Benjamin, New York, N. Y., 1964.

[6] R. J. Buenker and S. D. Peyerimhoff, *J. Phys. Chem.*, **73**, 1299 (1969).

[7] S. Rothenberg, P. Kollman, M. E. Schwartz, E. F. Hayes, and L. C. Allen, *Int. J. Quantum Chem., Symp.*, **3**, 715 (1970).

[8] J. L. Whitten, *J. Chem. Phys.*, **44**, 359 (1966).

[9] S. Huzinaga, *ibid.*, **42**, 1293 (1965).

[10] W. H. Fink, J. L. Whitten, and L. C. Allen, submitted for publication.

[11] See, for instance, L. C. Allen in "Quantum Theory of Atoms, Molecules and Solid State," P.-O. Löwdin, Ed., Academic Press, New York, N. Y., 1966, pp 39–80; S. D. Peyerimhoff and R. J. Buenker, *J. Chem. Phys.*, **47**, 1953 (1967); **45**, 734 (1966); R. J. Buenker, S. D. Peyerimhoff, L. C. Allen, and J. L. Whitten, *ibid.*, **45**, 2835 (1966); J. W. Moskowitz and M. C. Harrison, *ibid.*, **43**, 3550 (1965); W. H. Fink, *ibid.*, **49**, 5054 (1968).

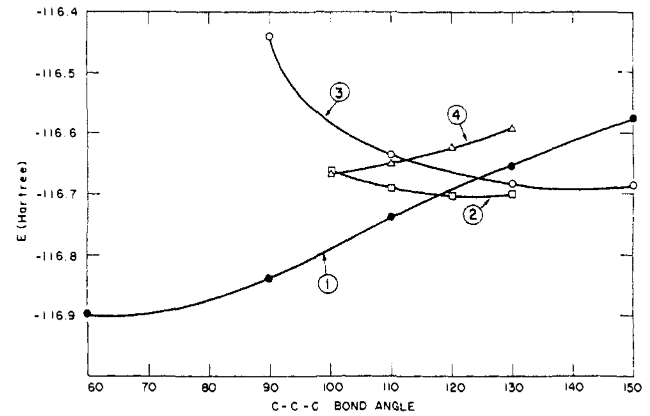

Figure 1. LCAO-MO-SCF total energies for cyclopropane as a function of C-C-C angle. Curve 1 is for the 90,90 form, electron configuration Φ_1. Curve 2 is for the 0,0 form, electron configuration Φ_2. Curve 3 is the 90,90 form, electron configuration ϕ_3. Curve 4 is for the 0,0 form, electron configuration Φ_4.

of the plane defined by the three carbon atoms. For the 90,90 geometry, the plane through the terminal methylene groups bisects the $C^{(1)}$-$C^{(3)}$-$C^{(2)}$ bond angle. This permits the 90,90 geometry to go over into the cyclopropane geometry at small $C^{(1)}$-$C^{(2)}$-$C^{(3)}$ bond angles. For the 0,0 geometry, the terminal methylene groups lie in the plane of the carbon skeleton. Here the lines through $C^{(1)}$,$C^{(2)}$, and $C^{(2)}$,$C^{(3)}$ bisect the H-C-H bond angles of the corresponding terminal methylenes.

Results and Discussion

The ground state of cyclopropane is known to be a $^1A_1$ state with the following electron configuration

$$\Phi_1 = (1a_1)^2(1b_2)^2(2a_1)^2(3a_1)^2(2b_2)^2(4a_1)^2(5a_1)^2\text{-}$$
$$(5a_1)^2(1b_1)^2(3b_2)^2(2b_1)^2(1a_2)^2(6a_1)^2(4b_2)^0 \quad (1)$$

Here the symbols a_1, a_2, b_1, and b_2 refer to the irreducible representations of the C_{2v} point group. Since the energies of the one-electron orbitals depend upon the geometry and the electron configuration, the ordering of the orbitals given in eq 1 is only approximate.

For the 0,0 and 90,90 geometries there are three other low-lying $^1A_1$ electron configurations which are particularly important. These configurations can be obtained by promoting two electrons from the $1a_2$, $6a_1$, or $2b_1$ orbitals to the $4b_2$ orbital. In this way one obtains

$$\Phi_2 = \ldots(1a_2)^2(6a_1)^2(2b_1)^0(4b_2)^2 \quad (2)$$

$$\Phi_3 = \ldots(1a_2)^2(6a_1)^0(2b_1)^2(4b_2)^2 \quad (3)$$

$$\Phi_4 = \ldots(1a_2)^0(6a_1)^2(2b_1)^2(4b_2)^2 \quad (4)$$

LCAO-MO-SCF calculations have been performed for each of these electron configurations at several $C^{(1)}$-$C^{(2)}$-$C^{(3)}$ bond angles for both the 0,0 and 90,90 geometries, using the basis sets described above. For the 90,90 case, the energies of configurations Φ_1 and Φ_3 are much lower than the energies of configurations Φ_2 and Φ_4, whereas for the 0,0 case, the reverse is true. In Figure 1, the variation of the total energy of configurations Φ_1 and Φ_3 is displayed as a function of the $C^{(1)}$-$C^{(2)}$-$C^{(3)}$ bond angle for the 90,90 geometry. Also shown in Figure 1 is the total energy of configurations Φ_2 and Φ_4 for the 0,0 geometry. Table I gives the calculated energy values.

With regard to Figure 1, the potential curves for Φ_1 and Φ_3 are very similar to those calculated by Buenker and Peyerimhoff[6] for the 90,90 orientation of the terminal methylene groups. There is a minimum on each of the two potential curves. On the potential curve for Φ_1, one finds the lowest energy of all at a $C^{(1)}$-$C^{(2)}$-$C^{(3)}$ bond angle of 60°. This is the cyclopropane minimum. The minimum on the curve Φ_3 occurs at a bond angle of approximately 140°. This energy minimum is similar to the 90,90 minimum found earlier for ethylene oxide.[12] Buenker and Peyerimhoff obtained this minimum for the Φ_3 curve at a somewhat smaller $C^{(1)}$-$C^{(2)}$-$C^{(3)}$ angle than ours, but they also find that the two curves for the 90,90 geometry intersect around 125°.[13] There is a minimum on each of the potential energy curves corresponding to Φ_2 and Φ_4. The interesting one is that on the Φ_2 curve for the 0,0 geometry, occurring at a $C^{(1)}$-$C^{(2)}$-$C^{(3)}$ bond angle of 125°. This corresponds to the trimethylene intermediate which Hoffmann discovered using extended Hückel theory.

As the $C^{(1)}$-$C^{(2)}$-$C^{(3)}$ bond angle increases, it is possible that the ground state may become a triplet state. Open-shell LCAO-MO-SCF calculations for the 90,90 case indicate that the $^3B_2$ state with the electronic configuration

$$\Phi_5 = \ldots(1a_2)^2(6a_1)^1(2b_1)^2(4b_2)^1 \quad (5)$$

is the lowest energy triplet. Similar calculations for the 0,0 geometry indicates that the $^3B_2$ state with the electronic configuration

$$\Phi_6 = \ldots(1a_2)^1(6a_1)^2(2b_1)^1(4b_2)^2 \quad (6)$$

is the lowest energy triplet. The variation of the energy of these states is also given in Table I. It is clear that the LCAO-MO-SCF results predict that the triplet states are the ground states at bond angles near 110°.

Table I. Sections through a CH_2-CH_2-CH_2 Potential Energy Surface[a]

C-C-C angle, deg	90,90 form Φ_1[b]	Φ_3	Φ_5 (triplet)	$\Phi_1 + \Phi_3$
60	−0.8974			
90	−0.8376	−0.4422	−0.7958	−0.8813
110	−0.7369	−0.6372	−0.8463	−0.8461
130	−0.6584	−0.6838	−0.8347	−0.8267
150	−0.5763	−0.6869	−0.7957	−0.7942
	0,0 form Φ_2	Φ_4	Φ_6 (triplet)	$\Phi_2 + \Phi_4$
100	−0.6645	−0.6670	−0.8391	−0.8355
110	−0.6924	−0.6497	−0.8491	−0.8470
120	−0.7028	−0.6243	−0.8456	−0.8464
130	−0.7017	−0.5928	−0.8323	−0.8367

[a] Energies reported in hartrees relative to −116 hartrees. For geometries, see text. [b] For definitions of electron configurations Φ_1-Φ_6, see eq 1-6.

In Table I, the two by two configuration-interaction results are reported for several 0,0 and 90,90 geometries. For the 90,90 geometries, configurations Φ_1 and Φ_3 were used, and for the 0,0 geometries the configurations

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(12) E. F. Hayes, *J. Chem. Phys.*, **51**, 4787 (1969).

(13) The differences between Buenker and Peyerimhoff's results (ref 6) and those reported here for the 90,90 form are mainly due to the use of somewhat different geometries.

Φ_2 and Φ_4 were used. The molecular orbitals from the lowest triplet were found to give a lower energy than the molecular orbitals from the singlet state. This is due to the inadequacy of the virtual orbitals. The results in Table I correspond to triplet molecular orbitals. Investigations of other $^1A_1$ configurations indicate that these configurations are much less important than the configurations considered here. On the basis of the two by two configuration-interaction calculations, the equilibrium $C^{(1)}$–$C^{(2)}$–$C^{(3)}$ bond angle for the 0,0 open form is predicted to be about 110°.

Owing to the crossing of the potential energy curves for Φ_1 and Φ_3, it might be expected that there would be a low-lying open 90,90 minimum. However, the two by two configuration-interaction calculations do not support this expectation. In fact, more extensive CI calculations on the 90,90 form reported by Buenker and Peyerimhoff[6] show no minimum in the large-bond-angle region. However, in order to definitely decide whether a stable minimum for the open 90,90 form exists, it will probably be necessary to investigate changes in carbon–carbon bond length, since configuration Φ_3 is more bonding in the $C^{(1)}$–$C^{(2)}$ and $C^{(2)}$–$C^{(3)}$ bonds than configuration Φ_1; this suggests that the optimal carbon–carbon bond length for the 90,90 open form should be shorter than the carbon–carbon bond length for cyclopropane.

The rotational barriers for concerted and nonconcerted rotation of the terminal methylene groups are very important, since the 0,0 open form is thought to undergo concerted ring closure to form cyclopropane.[4] In studying the nonconcerted rotational barrier, it was found that the most stable electron configuration for the 0,90 intermediate is an open-shell singlet

$$\Phi_7 = (1a')^2(2a')^2(3a')^2(4a')^2(5a')^2(6a')^2(7a')^2\text{-}$$
$$(1a'')^2(8a')^2(2a'')^2(9a')^2(3a'')^1(10a')^1 \quad (7)$$

rather than a closed-shell singlet such as

$$\Phi_8 = \ldots(9a')^2(3a'')^2(10a')^0 \quad (8)$$

or

$$\Phi_9 = \ldots(9a')(3a'')^0(10')^2 \quad (9)$$

Here the symbols a′ and a′′ refer to the two irreducible representations of the C_s point group. Since the open-shell program which is in MOLE cannot be used for open-shell singlets, the molecular orbitals from the corresponding triplet were used to calculate the energy of the open-shell singlet corresponding to Φ_7. Configuration-interaction calculations with the open-shell singlet indicate that there are no other low-lying states which couple strongly with Φ_7, whereas this is not the case in connection with the pairs $[\Phi_1,\Phi_3]$ and $[\Phi_2,\Phi_4]$. Thus, for a $C^{(1)}$–$C^{(2)}$–$C^{(3)}$ bond angle of 110°, these calculations for the 0,0 form predict a rotational barrier of 2.5 kcal/mol for the singlet state and less than 1 kcal/mol for the triplet state. For the 90,90 form the rotational barrier for the singlet is 1.5 kcal/mol and the barrier for the triplet is again less than 1 kcal/mol. One would like to know the difference between the barriers for concerted rotation and nonconcerted rotation of the terminal methylene groups. Unfortunately, the barrier for concerted rotation is probably smaller than the barrier for nonconcerted rotation. This means that both barriers are small compared to the accuracy of the calculations. For this reason the barrier for concerted rotation was not investigated.

It is difficult to know how reliable the predicted barriers for nonconcerted rotation of the terminal methylene are. Previous studies of rotational barriers have been quite successful.[14] However, there are two important features of the trimethylene barriers which were not present in the earlier studies. First, the features of the electronic structure which are important for the trimethylene barrier distinguish it from other rotational barriers such as ethane which have been studied previously by nonempirical methods. Moreover, there do not seem to be any similar cases which have been studied experimentally. Secondly, there are special difficulties in the selection of the geometry and the level of approximation. Changes in the C–C bond length, the H–C–H bond angles, and the orientation of the terminal methylene groups will certainly be necessary before quantitatively meaningful results can be obtained. Furthermore, the basis set may not be sufficient for this study even though it has been useful in the past.[11] It is also clear that the two by two mixing of electron configurations Φ_1 and Φ_3, and of Φ_2 and Φ_4, only accounts for part of the correlation energy, and other types of correlation energy may be equally important. Unfortunately, this problem of going beyond the LCAO–MO–SCF method to obtain quantitatively meaningful results is complicated, since there are many configurations which need to be considered. Currently, this problem is being investigated in this laboratory. However, it does not seem likely that one will be able to obtain results which are significantly better than Siu and Davidson's[15] results for CO. To our knowledge, this is the best calculation to date on a molecule as large as CO. This would mean that the total energy of trimethylene would be 100–200 kcal/mol from the true Born–Oppenheimer result. Even if this calculation is carried out with optimization of the geometry, the calculated rotational barrier may be off as much as 5 or 10 kcal/mol. Therefore, unless one finds a prototype system for which the experimental barrier is known, even this level of approximation cannot be checked. For this reason, it does not seem likely that a definitive calculation of the rotation barrier in trimethylene is possible with the methods which are currently available.

Owing to the unique features of the trimethylene barrier mentioned above, it appears that no definite decision about the precise nature of the intermediates involved in the isomerization of cyclopropane and the formation of cyclopropane from pyrazolines can be determined with nonempirical calculations at this time. Nevertheless, there can be little doubt that there is a minimum corresponding to the 0,0 open form of cyclopropane, as suggested by Hoffmann.[4] However, it is still not clear whether this species is an intermediate in either the isomerization of cyclopropane or the pyrolysis of pyrazolines to give cyclopropane.

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(14) For summaries of previous barrier calculations, see J. P. Lowe, *Progr. Phys. Org. Chem.*, 6, 1 (1968).

(15) A. K. Q. Siu and E. R. Davidson, *Int. J. Quantum Chem.*, 4, 223 (1970).

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An Experimental Comparison of the Theories of Elasticity of Polymer Networks

J. E. Mark

Contribution from the Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48104. *Received June 11, 1970*

Abstract: The three main theories of rubberlike elasticity yield expressions for the elastic free energy of a network made up of Gaussian chains which differ significantly with respect to a volume-dependent contribution to the entropy. In the present study, the validity of each of these theoretical expressions is gauged by measuring the ratio of the moduli of two networks of *cis*-1,4-polybutadiene which have the same equilibrium extent of swelling but differ markedly in the volume at which the chemical cross-links had been introduced: one series of samples had been cross-linked in the bulk (undiluted) state, another in dilute solution to the syneresis point. The relationship derived by Hermans is shown to be inconsistent with the existence of syneresis and thus is clearly unacceptable. Neither the theory of James and Guth nor that of Flory and coworkers succeeds in predicting the magnitude of the ratio of the moduli or its dependence on the degree of cross-linking. Of the networks studied, those formed in solution showed significantly smaller departures from the predicted form of the dependence of stress on strain and considerably smaller nonequilibrium, relaxation effects. These differences are used to provide a qualitative interpretation of the discrepancies between theory and experiment in terms of network topology.

The foundations of the statistical-mechanical theory of the elasticity of polymer networks have been laid by three main groups of workers, namely by James and Guth,[1-6] by Wall and Flory and coworkers,[7-14] and by Hermans.[15,16] In independent, theoretical investigations these groups have obtained expressions for the crucially important entropy of network deformation which differ with respect to the existence and magnitude of a volume-dependent contribution. Extensive discussions[5,6,11,15,16] of this point of contention have not brought about agreement, and the controversy has continued to the present time.

Experimental evidence bearing on this problem is sparse, because the contested entropic contribution does not affect the predicted elastic equation of state, the fundamental equation of rubber elasticity which relates a network's retractive force to its extent of deformation, temperature, and structure. The equations, however, which relate the extent of swelling of a network in contact with an excess of solvent to its density of cross-links are markedly different in the three theories. This predicted difference has served as a basis for several attempts[17-19] to determine which of the present theories is most nearly correct. The results have been ambiguous and have not definitely supported any one theory. Furthermore, the independent measure of the effective cross-link density of the network which is required for the interpretation of some of the measurements was obtained by assuming the chemical cross-linking agent reacted stoichiometrically with the polymer to form a highly idealized structure. This is an exceedingly poor assumption for a number of reasons, including the possible loss of reagent in side reactions and the formation of network defects which are ineffective in the elastic response of the network.[20,21]

It is the purpose of the present study to attempt to evaluate definitively the several theories by means of measurements of both moduli and extents of swelling of networks prepared under conditions carefully chosen so as to maximize the differences between the predictions of the various theories.

Theory

According to the most general versions[3,13,16] of the theory of rubberlike elasticity, the change ΔA_{el} in the Helmholtz free energy resulting from the deformation of a network of chains having a Gaussian distribu-

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(1) E. Guth and H. M. James, *Ind. Eng. Chem.*, **33**, 624 (1941).
(2) H. M. James and E. Guth, *ibid.*, **34**, 1365 (1942).
(3) H. M James and E. Guth, *J. Chem. Phys.*, **11**, 455 (1943).
(4) H. M. James and E. Guth, *ibid.*, **15**, 669 (1947).
(5) H. M. James and E. Guth, *J. Polym. Sci.*, **4**, 153 (1949).
(6) H. M. James and E. Guth, *J. Chem. Phys.*, **21**, 1039 (1953).
(7) F. T. Wall, *ibid.*, 10, 132, 485 (1942); **11**, 527 (1943).
(8) P. J. Flory and J. Rehner, Jr., *ibid.*, **11**, 512, 521 (1943).
(9) P. J. Flory, *Chem. Rev.*, **35**, 51 (1944).
(10) P. J. Flory *J. Chem. Phys.*, **18**, 108, 112 (1950).
(11) F. T. Wall and P. J. Flory, *ibid.*, **19**, 1435 (1951).
(12) P. J. Flory, *J. Amer. Chem.Soc.*, **78**, 5222 (1956).
(13) P. J. Flory, C. A. J. Hoeve, and A. Ciferri, *J. Polym. Sci.*, **34**, 337 (1959).
(14) P. J. Flory, *Trans. Faraday Soc.*, **57**, 829 (1961).
(15) J. J. Hermans, *ibid.*, **43**, 591 (1947).
(16) J. J. Hermans, *J. Polym. Sci.*, **59**, 191 (1962).
(17) A. M. Rijke and W. Prins, *ibid.*, **59**, 171 (1962); B. Mukherji and W. Prins, *ibid.*, *Part A*, **2**, 4367 (1964).
(18) G. Gee, J. B. M. Herbert, and R. C. Roberts, *Polymer*, **6**, 541 (1965).
(19) A. M. Rijke and G. L. Taylor, *J. Polym. Sci.*, *Part A-1*, **5**, 1433 (1967).
(20) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953.
(21) L. R. G. Treloar, "The Physics of Rubber Elasticity," Oxford University Press, London, 1958.