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References and Notes

(1) (a) Part 29 of this series: M. Raban and G. Yamamoto, *J. Org. Chem.*, **40,** 3093 (1975); (b) We thank the National Science Foundation, the National Institutes of Health, and the E. de Rothschild Foundation for support of this research. (c) Preliminary accounts of this work have appeared: D. Kost, W. Stacer, and M. Raban, *J. Am. Chem. Soc.*, **94,** 3233 (1972); M. Raban and D. Kost, *ibid.*, **94,** 3234 (1972).

(2) (a) Department of Chemistry, Ben-Gurion University of the Negev, Beersheva Israel; (b) A. P. Sloan Fellow, 1972–1976.

(3) (a) S. Wolfe, A. Rauk, L. M. Tel, and I. G. Csizmadia, *J. Chem. Soc. B*, 136 (1971); (b) F. Bernardi, I. G. Csizmadia, A. Mangini, H. B. Schlegel, M.-H. Whangbo, and S. Wolfe, *J. Am. Chem. Soc.*, **97,** 2209 (1975); (c) E. L. Eliel, *Angew. Chem., Int. Ed. Engl.*, **11,** 739 (1972); (d) K. Muller, *Helv. Chem. Acta*, **53,** 1112 (1970); (e) G. Baddeley, *Tetrahedron Lett.*, 1645 (1973); (f) R. C. Bingham, *J. Am. Chem. Soc.*, **97,** 6743 (1975); (g) D. Kost and M. Raban, *J. Org. Chem.*, **41,** 1748 (1976).

(4) Reviews: (a) J. M. Lehn, *Fortschr. Chem. Forsch.*, **15,** 311 (1970); (b) A. Rauk, L. C. Allen, and K. Mislow, *Angew. Chem., Int. Ed. Engl.*, **9,** 400 (1970); (c) M. Kessler, *ibid.*, **9,** 219 (1970); (d) J. B. Lambert, *Top. Stereochem.*, **6,** 19 (1971).

(5) (a) M. Raban, G. W. J. Kenney, Jr., and F. B. Jones, Jr., *J. Am. Chem. Soc.*, **91,** 6677 (1969); (b) M. Raban and F. B. Jones, Jr., *ibid.*, **93,** 2692 (1971).

(6) R. C. Cookson, T. A. Crabb, J. J. Frankel, and H. Hudec, *Tetrahedron, Suppl., No.* **7,** 355 (1966).

(7) (a) H. Saito, K. Nukada, T. Kobayashi, and K. Morita, *J. Am. Chem. Soc.*, **89,** 6605 (1967); (b) S. J. Brois, *Trans. N.Y. Acad. Sci., Ser. II*, **31,** 937 (1969).

(8) J. Kay, M. Glick, and M. Raban, *J. Am. Chem. Soc.*, **93,** 5224 (1971).

(9) (a) J. M. Lehn and J. Wagner, *Chem. Commun.*, 1298 (1968); (b) F. A. L. Anet, R. D. Trepka, and D. J. Cram, *J. Am. Chem. Soc.*, **89,** 359 (1967).

(10) (a) L. P. Hammett, "Physical Organic Chemistry", 2d ed, McGraw-Hill, New York, N.Y., 1970; (b) H. H. Jaffe, *Chem. Rev.*, **53,** 191 (1953).

(11) Hammett substituent constants were taken from ref 10b.

(12) J. D. Andose, J.-M. Lehn, K. Mislow, and J. Wagner, *J. Am. Chem. Soc.*, **92,** 4050 (1970).

(13) T. Jordan, H. W. Smith, L. L. Lohr, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **85,** 846 (1963).

(14) M. D. LaPrade and C. E. Nordman, *Inorg. Chem.*, **8,** 1669 (1969); E. D. Morris and C. E. Nordman, *ibid.*, **8,** 1673 (1969).

(15) I. G. Csizmadia, A. H. Cowley, M. W. Taylor, and S. Wolfe, *J. Chem. Soc., Chem. Commun.*, 432 (1974).

(16) J. Hirsch, *Top. Stereochem.*, **1,** 199 (1967).

(17) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry", M. S. Newman, Ed., Wiley, New York, N.Y., 1956, Chapter 13.

(18) The E_s value for CF_3 is only slightly larger than the value of 1.1 which can be estimated for E_s (C_6H_5) by considering that the value for phenyl should exceed that for cyclohexyl by about the same amount that the *A* value for phenyl exceeds that for cyclohexyl.

(19) J. Bystrov, R. G. Kostyanovskii, O. A. Panshin, A. U. Stepanyants, and O. A. Yuzhakova, *Opt. Spectrosc. (USSR)*, **19,** 122, 217 (1965).

(20) For discussion of σ–π conjugation (and its effects on barriers to nitrogen inversion) see: (a) Reference 4: (b) R. D. Bach and P. A. Scheer, *J. Am. Chem. Soc.*, **94,** 220 (1972); (c) R. D. Baechler and K. Mislow, *J. Chem. Soc., Chem. Commun.*, 185 (1972).

(21) M. Raban, D. A. Noyd, and L. Bermann, *J. Org. Chem.*, **40,** 752 (1975).

(22) (a) F. G. Riddell, J. M. Lehn, and J. Wagner, *Chem. Commun.*, 1403 (1968); (b) D. L. Griffith and B. L. Olson, *ibid.*, 1682 (1968); (c) M. Raban, F. B. Jones, Jr., E. H. Carlson, E. Banucci, and N. A. LeBel, *J. Org. Chem.*, **35,** 1496 (1970).

(23) (a) D. Kost and A. Zeichner, *Tetrahedron Lett.*, 3239 (1975); (b) F. A. Davis and E. W. Kluger, *J. Am. Chem. Soc.*, **98,** 302 (1976).

(24) T. L. Cairns, *J. Am. Chem. Soc.*, **63,** 871 (1941).

Vapor-Phase Structure and Conformation of a Long-Chain *n*-Alkane. An Electron Diffraction Study

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Abstract: The structure of *n*-hexadecane has been determined at a nozzle temperature of 150 °C by gas-phase electron diffraction. Molecular parameters, averaged over the diverse conformers present, were found to be $(\pm 3\sigma) r_g$(C–C) = 1.542 ± 0.004 Å, r_g(C–H) = 1.130 ± 0.008 Å, ∠CCC = 114.6 ± 0.6°, ∠CCH = 110.4 ± 1.1°, gauche CCCC dihedral angle = 64.9 ± 10°, and $\Delta G°$ (the gauche-trans free energy difference per gauche link) = 275 ± 350 cal/mol. Amplitudes of vibration were also measured. The average C–C bond is 0.01 Å longer than C–C bonds reported in short-chain vapor-phase *n*-alkanes. This increase is interpreted as indicating a difference between interior methylene–methylene bonds and bonds at or near a chain end. Other evidence, including ab initio and potential energy minimization calculations, is cited in support of such an effect of environment on bond length. The diffraction data also suggest site-to-site variations in structure consistent with a picture in which gauche $CH_2 \cdots CH_2$ steric interactions deform local CCC bond angles and trans CCCC dihedral angles. A value for the characteristic ratio of condensed polymethylene was calculated, based on the *n*-hexadecane vapor-phase parameters and a three-state model. The result, 7.9 ± 2 (3σ), agreed with the experimental value of 6.8 ± 0.3 to within experimental error.

Information about the structure and rotational isomerization of hydrocarbon chains is of concern to chemists in varied areas of research. Extensive studies have been made of the structures of both short and long chains as they exist in crystals, constrained to be in their all-trans form. Only a few investigations of the structures and conformational energy differences of free vapor-phase hydrocarbon chains have been published and, heretofore, these have been carried out on relatively short *n*-alkanes (*n*-heptane or shorter).[1-3] Because the short chains appear to possess very similar structures and conformational energy differences, it has been often assumed, in the absence of other information, that average bond lengths, angles, and gauche-trans energy differences are independent of the chain length. In view of the fact that long hydrocarbon chains commonly occur in compounds of concern to chemists and biologists, it was of interest to learn from electron diffraction studies that this assumption may not be quantitatively valid. Therefore, we report our findings for *n*-hexadecane, a considerably longer chain hydrocarbon than has previously been studied in the vapor phase.

Experimental Section

A sample of *n*-hexadecane with a stated purity of 99 mol % was obtained from the Aldrich Chemical Co. and was used without further purification. The sample was heated to 150 °C in a nozzle furnace of Hargittai's design[4] to provide a pressure[5] of 23 Torr [1 Torr = (101.325/760) kPa]. Scattering patterns provided by 40 kV incident electrons were obtained at the 21-, 11-, and 7-cm camera distances through a rotating r^3 sector and at the 21-cm distance through a rotating r^2 sector. Diffraction patterns were recorded on 4 × 5 in. Kodak Electron Image plates using the University of Michigan apparatus.[6] Experimental conditions are summarized in Table I.

Table I. Experimental Conditions under which Diffraction Patterns of *n*-Hexadecane Were Recorded

	I	II	III	IV
Camera distance, cm	21.538	21.550	10.472	6.035
Sector (radius, cm)	r^2 (3.2)	r^3 (4.8)	r^3 (4.8)	r^3 (4.8)
Sample temperature, °C	150	150	150	150
Sample pressure, torr	15	15	15	15
Exposure time, s	1.5	9	40	90
Beam currents, μA	0.700	0.728	0.700	
Nozzle throat diameter, cm	0.041	0.041	0.041	0.041
Nozzle lip to beam dist, cm	0.100	0.18	0.17	0.18
Electron wavelength, Å	0.06015	0.06015	0.06015	0.06015
Number of plates	5	5	5	4

Voltages proportional to the photographic densities were measured with the automated microphotometer and recording system described elsewhere.[6] The derived absorbances, A, were then converted to relative intensities, E, via the relationship[7]

$$E = A(1 + 0.116A + 0.017A^2 + 0.003\,12A^3) \qquad (1)$$

Four or five plates from each camera distance were chosen, and the intensities for each group were averaged together. These were transformed to leveled intensities, $I_0(s)$, in the conventional manner, using the partial wave elastic and inelastic scattering factors tabulated by Schafer, Yates, and Bonham.[8] The experimental s and $I_0(s)$ values, as well as the interpolated s, $I_0(s)$, and background functions, $I_B(s)$, used in the analysis are given in the supplementary material.

Molecular Model

n-Hexadecane is too large a molecule to analyze without introducing simplifications into the molecular description. A molecule of *n*-hexadecane has 1225 internuclear distances in a given conformation and can exist in well over a million conformations. Therefore, it was necessary to formulate a statistical model structure with mean bond lengths, angles, amplitudes of vibration, and a mean gauche-trans free energy difference.

Five independent geometrical parameters were chosen to characterize the structure. These were the average C–C and C–H bond lengths, the average CCC and HCH bond angles, and the average gauche CCCC dihedral angle. All trans dihedral angles were fixed at 180° (torsional and other shrinkage corrections were made, however). All methylene groups were assumed to possess local C_{2v} symmetry. Configurations containing gauche$^+$-gauche$^-$ sites were excluded. The excess free energy of a configuration containing a multiple number n of gauche sites was assumed to be equal to n times the excess free energy of a single gauche site (i.e., $\Delta G°_{gg} = 2\Delta G°_g$, etc.), independent of the environment of the gauche site.

Many of the longer internuclear distances in *n*-hexadecane correspond to very broad peaks in the radial distribution function and therefore may be neglected in an analysis concerned with short-range structural features. Since the shortest 1,7-C···C distance was 5.0 Å, had a low multiplicity, and exhibited a large amplitude of vibration, it seemed unprofitable to retain C···C contributions more remote than 1,7. In initial stages of the refinement, no C···H or H···H contributions beyond 1,5 were considered. Once the values of the independent parameters had been fairly well determined, the intensity arising from the many 1,6- and 1,7-C···H distances were computed for several different values of the gauche-trans free energy difference. Since it would have been expensive and of minor import to refine these distances simultaneously with the other parameters, their diffraction contributions were subtracted from the total molecular intensity to reduce possible interferences with C···C diffraction features. The independent parameters were then refined by least squares. Only a marginal improvement in agreement between calculated and observed intensities resulted, and the parameters themselves did not change significantly, showing that the neglect of C···H and H···H contributions from beyond 1,5 is justified.

A model which allowed the explicit specification of all C···C distances through 1,7 and all C···H and H···H distances through 1,5 was devised. Multiplicities of the C···C distances were obtained from the assumed values of $\Delta G°$(gauche-trans). The multiplicities of the various 1,7 distances were determined from the ratio of gauche-containing conformations to the all trans conformation, which is dependent upon $\Delta G°$ according to the relationship

$$\%\ \text{gauche}/\%\ \text{all trans} = M \exp(-n\Delta G°/RT) \qquad (2)$$

where M is the number of ways a given gauche-containing configuration can occur in a chain (for example, the configuration TGTG can occur in eight different ways) and n is the number of gauche sites contained in that configuration. Again, conformations containing gauche$^+$-gauche$^-$ sites were considered too improbable to be taken into account. The M values used in eq 2 for the various 1···7 distances were the multiplicities of the various *n*-heptane configurations given in ref 3. Due to the constraints imposed by the disallowance of the gauche$^+$-gauche$^-$ configuration, it was necessary to adopt a reference segment length to give a basis for determining the multiplicities of the various 1,4- through 1,7-C···C distances. For simplicity, a 7-carbon segment rather than the full 16-carbon skeleton was chosen. Multiplicities computed by taking 8- or 10-carbon segments were so similar to those computed on the 7-carbon basis that it seemed unjustified to go to a more complex analysis. Multiplicities for the C···H and H···H distances were determined from the multiplicities of the various skeletal rotational configurations.

The rigid exclusion of gauche$^+$-gauche$^-$ configurations cannot be quantitatively correct. However, calculations performed with the model force field MUB-2,[9] which is based upon carefully calibrated nonbonded interactions, indicate that this severely strained configuration imparts a strain energy of about 3 kcal/mol in addition to $2\Delta G°$. Therefore, the influence of the exclusion of gauche$^+$-gauche$^-$ on the values determined for the C···C multiplicities may be assumed to be small. In chains much longer than C_{16} where a sharp bend may be stabilized by a favorable packing of one chain segment against another, the above exclusion would be too restrictive and chain–chain interactions would vitiate eq 2.

The assumption of a 7-carbon skeleton as the basis upon which the C···C multiplicities are calculated introduces a systematic error into the value determined for $\Delta G°$, causing it, in the absence of any other perturbing factors, to be slightly overestimated. However, the assumption that the free energy of a gauche conformation is site independent probably introduces at least as large an error (of unknown sign) into the $\Delta G°$ value as does the use of the 7-carbon basis.

Analysis of Data

After intensities from each camera distance were subjected to preliminary least-squares analysis to arrive at background functions, the data from the various camera distances were blended, yielding a smooth molecular intensity curve ranging from $s = 2.20$ to 46.81. Weights proportional to s were used throughout the least-squares analyses. The $s^{1/2}$-weighted residuals were evenly distributed throughout the data space, indicating that the weight matrix adopted was reasonable. A succession of least-squares analyses of the intensity data was performed, adopting different fixed values of $\Delta G°$. The value chosen for $\Delta G°$ had a negligible effect upon the values derived for the structural parameters, but an appreciable effect on the

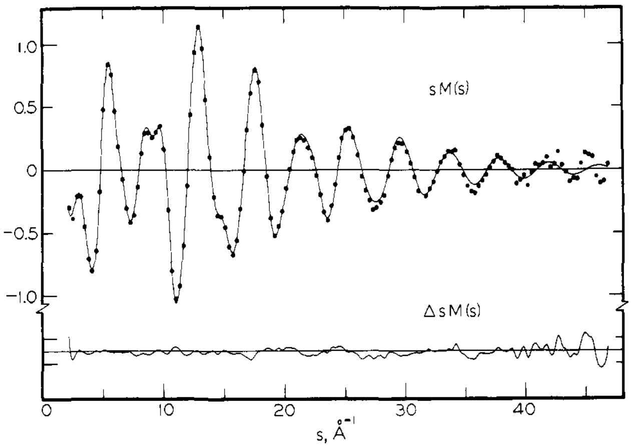

Figure 1. Reduced molecular intensity curves for n-hexadecane. Points, experimental; solid line, theoretical. $\Delta sM(s)$ is experimental − theoretical.

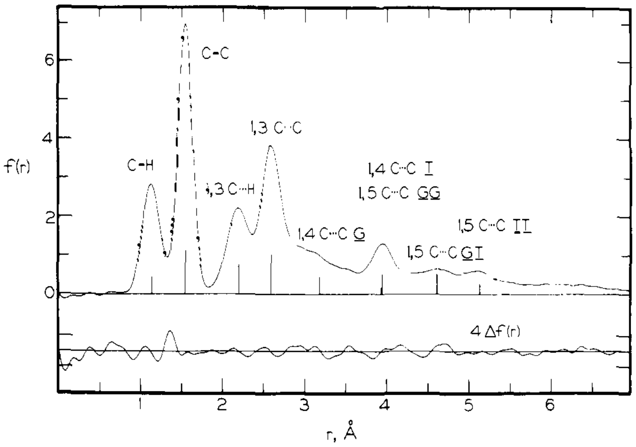

Figure 2. Experimental radial distribution curve for n-hexadecane. $\Delta f(r)$ is experimental − theoretical.

Table II. Mean Molecular Parameters and Estimated Errors (3σ) for n-Hexadecane

Parameter	r_g^{exptl}	l_g^{exptl}	$l_{(\text{butane})}^{\text{calcd } b}$
C–C	1.542 (4)	0.057 (5)	0.051
C–H	1.130 (8)	0.087 (10)	0.079
1,3-C···C	2.587 (5)[c]	0.086 (11)	0.077
1,3-C···H	2.201 (8)[c]	0.121 (11)	0.110
1,4-$(\text{C}\cdots\text{C})_{\text{gauche}}$	3.186 (51)[c]	0.216 (51)	0.201
1,4-$(\text{C}\cdots\text{C})_{\text{trans}}$	3.940 (7)[c]	0.097 (12)[d]	0.077
∠CCC	114.6 (.6)	∠HCH	99.5 (4.5)
∠CCH	110.4 (1.1)	Gauche dihedral angle	65 (10)
Index of resolution	0.97, 0.90, 0.95, 0.86		
Camera dist (sector)	21 (r^2), 21 (r^3), 11 (r^3), 7 (r^3)		
$\sigma(I)/\langle I\rangle = 0.0018$			
Site-to-site variations: see text			

[a] Distances in Å, angles in deg. [b] Based on field of ref 23, as applied in ref 7; at 420 K. [c] Uncertainties do not include uncertainties in shrinkages adopted. [d] Parameter not refined simultaneously with others; trial and error estimate.

fit of the intensity function. The best value of $\Delta G°$ was taken to be that yielding the minimum value of $\sigma(I)$.

Far too many distances occur in the observed region of the radial distribution curve to permit the determination of all amplitudes of vibration. The mean bonded C–C and C–H, 1,3-C···C and C···H, and 1,4 gauche C···C, amplitudes were varied freely along with the previously specified independent structural parameters. Amplitudes for the other distances were not varied along with the independent parameters but were assigned plausible values. Initially, sets of amplitudes were derived from analogous n-butane values[10] and from Mastryukov and Cyvin's formulas for computing C···C and C···H amplitudes.[11] Later, the 1,4-*trans*-C···C and the average 1,5- and greater C···C, 1,4-C···H, and 1,3-H···H amplitudes were allowed to vary once a good structure for a given value of $\Delta G°$ had been obtained, but these were never varied in concert with the independent parameters. Values for shrinkage corrections applied to the various internuclear distances were estimated by rough extrapolations from related values determined for n-butane.[7] Morse asymmetry constants of 2.0 Å^{-1} were adopted for all distances. In the final stages of the analysis, once the values for the primary parameters were well established, certain amplitudes and shrinkages were adjusted by hand to reduce residuals in the radial distribution curve. The shrinkages and assumed or marginally determined amplitudes used in the analysis are given in the microfilm edition.

Results

Structural Parameters. Table II lists the values determined for the independent parameters and their estimated limits of error. The limits of error reported (except for the gauche dihedral angle) are three times the least-squares standard deviations corrected (approximately) for the effects of correlation of the weighted residuals according to the formulation of Bartell and Anashkin,[12] eq 9. A γ value of 1 Å was used. The error limit given for the average gauche CCCC dihedral angle should be regarded as a plausible subjective estimate; the dihedral angle parameter was correlated with some of the amplitudes (notably the 3.5 Å C···H amplitude) and shrinkages which were not varied freely. Elements of the correlation matrix are listed in Table III. The values given in Tables II and III were determined assuming $\Delta G° = 296$ cal/mol (a value very close to the best value). Figure 1 shows the blended molecular intensity function and residuals while Figure 2 shows the corresponding radial distribution curve, again for $\Delta G° = 296$ cal/mol.

The best value of $\Delta G°$ was found to be 275 cal/mol as described in the previous section. Figure 3 compares the experimental and theoretical radial distribution curves, computed for various values of $\Delta G°$, in a region sensitive to the conformational composition. Visual inspection of Figure 3 reinforces the least-squares result for $\Delta G°$ in suggesting a value between 296 and 185 cal/mol [i.e., $\exp(-\Delta G°/RT)$ between 0.7 and 0.8] but it also reveals the limited sensitivity of the electron diffraction method for this particular parameter. A statistical limit of error of ±250 cal/mol for $\Delta G°$ was estimated from the curvature of $\sigma(I)$ as a function of $\Delta G°$; however, this value does not reflect the effects of the slight model dependence exhibited by the $\sigma(I)$ or the approximations implicit in the molecular model. Hence, a more reasonable estimate of the limits of error for the $\Delta G°$ value is ±350 cal/mol. The experimental value may be compared with the average value of 500 ± 220 cal/mol ($\sim 3\sigma$) for butane through heptane determined by electron diffraction.[10] Model field MUB-2 applied to the six gauche-containing conformers of n-hexane (each fully relaxed) yields an average value for $\Delta E°$ per gauche link of 609 cal/mol (a priori weights) and a site-to-site scatter characterized by a 98 cal/mol standard deviation.[25]

Calculation of the Characteristic Ratio of Polymethylene. n-Hexadecane may be regarded as a "micro-polymer" with

Table III. Correlation Matrix for *n*-Hexadecane[a]

	$r_{C\text{-}C}$	$r_{C\text{-}H}$	∠CCC	½∠HCH	τ_{CCCC}(G)	$l_{C\text{-}C}$	$l_{C\text{-}H}$	$l_{1,3\text{-}CC}$	$l_{1,3\text{-}CH}$	$l_{1,4\text{-}CC_{gauche}}$	R^b
σ^c	0.641	1.67	0.132	0.515	1.65	0.770	1.73	1.90	2.43	14.5	0.00932
	1.000	0.068	−0.481	0.222	0.084	0.118	0.099	0.055	0.019	−0.140	0.158
		1.000	−0.009	0.408	−0.027	−0.020	0.087	−0.007	0.010	−0.081	0.025
			1.000	−0.360	0.060	−0.049	−0.041	−0.042	0.097	0.080	−0.070
				1.000	−0.022	0.179	0.148	0.216	−0.007	−0.241	0.343
					1.000	0.030	0.015	0.189	−0.029	−0.302	0.039
						1.000	0.193	0.211	0.106	−0.167	0.594
							1.000	0.124	0.064	−0.108	0.354
								1.000	0.085	−0.109	0.358
									1.000	−0.065	0.184
										1.000	−0.282
											1.000

[a] From zero-order error matrix, notation of ref 12, $\Delta G°$ fixed at 296 cal/mol. [b] Index of resolution. [c] Zero-order standard deviations, distances *r* and *l* in thousandths of an Å unit, angles in deg, *R* is dimensionless.

a chemical composition homologous to that of polymethylene. It is instructive to examine whether structural properties of free *n*-hexadecane molecules can be used to infer related properties of polymers in condensed phases. One polymer parameter offering a particularly appropriate basis for comparison is the characteristic ratio.

The characteristic ratio is defined as $\langle r^2\rangle_0/nl^2$, where $\langle r^2\rangle_0$ is the mean-square distance between the two ends of the chain, corrected for the effects of excluded volume, *n* is the number of segments in the polymer chain, and *l* is the length of each segment. The characteristic ratio usually approaches a constant for a statistical distribution of chain conformers of a given polymer as the chain length increases. Experimental values of the characteristic ratio may be determined from light scattering and solution viscosity measurements. A theoretical value may be computed from average structural parameters and conformational free energy differences according to a simple three-state statistical model as formulated by a number of researchers. Abe, Jernigan, and Flory have published a calculation of this type for polymethylene,[13] using structural parameters and a gauche-trans free energy difference obtained from experimental studies on small *n*-alkanes. The only necessary parameter not available from experiment, the (gauche$^+$-gauche$^-$) − (gauche$^+$-gauche$^+$) free energy difference (hereafter referred to as $\Delta G°_{g^+g^-}$), was computed with the aid of a model force field parameterized to reproduce the assumed *n*-butane gauche-trans free energy difference to 500 cal/mol. Because *n*-hexadecane is expected to be more like polymethylene than are the shorter *n*-alkanes, and since MUB-2 is a more highly parameterized and extensively tested model force field than is the one used by Abe, Jernigan, and Flory, it was of interest to recalculate the characteristic ratio from this newer information.

MUB-2 calculations on *n*-nonane suggest a value of 3 kcal/mol for $\Delta G°_{g^+g^-}$. With this information and Hoeve's formula for the characteristic ratio of a chain of infinite length,[14] the only parameters needed from the *n*-hexadecane structure study were the average CCC bond angle, gauche CCCC dihedral angle, and gauche-trans free energy difference. The trans dihedral angle was taken to be 180°, which value had been assumed throughout the structure determination. Calculation of the characteristic ratio with a CCC angle of 114.5°, a *gauche* CCCC angle of 65°, $\Delta G°$(gauche-trans) equal to 275 cal/mol, and $\Delta G°_{g^+g^-}$ equal to 3 kcal/mol gives a value of 7.9, which may be compared with the experimental value of 6.8 ± 0.3.[15] Since the limit of error of the computed value resulting from the propagation of the estimated limits of error of the CCC angle, the gauche CCCC angle, and $\Delta G°$ (gauche-trans) is ±2, the difference between the computed and experimental values is not significant.

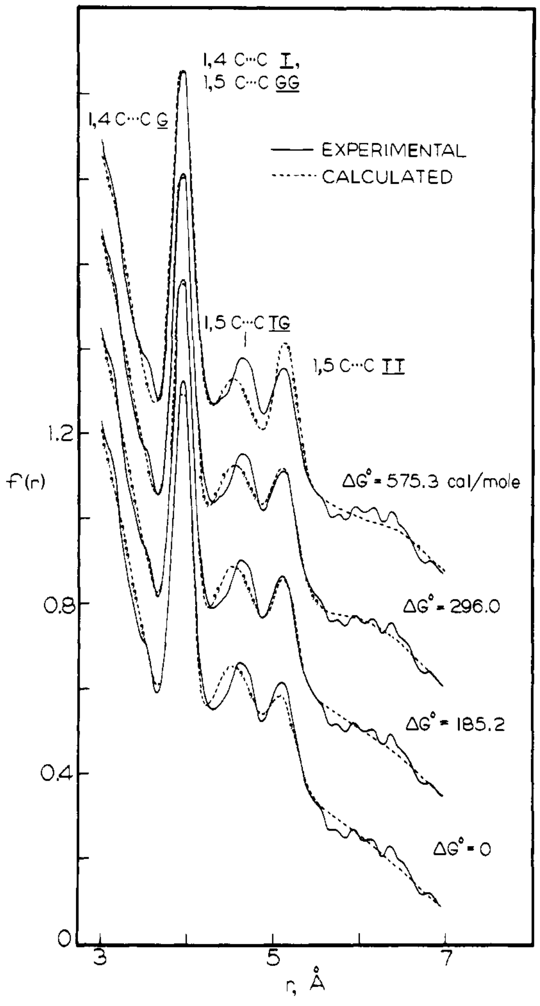

Figure 3. Experimental and calculated radial distribution curves for the region sensitive to $\Delta G°$, the mean free energy difference between gauche and trans conformations in *n*-hexadecane. The vertical *f*(*r*) scale shown applies to the lowest curve.

Discussion

Characteristic Ratio. The results of the characteristic ratio calculation are somewhat inconclusive. Abe, Jernigan, and Flory computed a slightly lower value for the characteristic ratio (7.6 according to the three-state model) from the small *n*-alkane data than we obtained from the *n*-hexadecane and MUB-2 data. Among the small alkane parameters adopted by Flory et al. (112°, 65°, 500 cal/mol, and 2 kcal/mol for the average CCC angle, gauche CCCC angle, $\Delta G°$(gauche-trans),

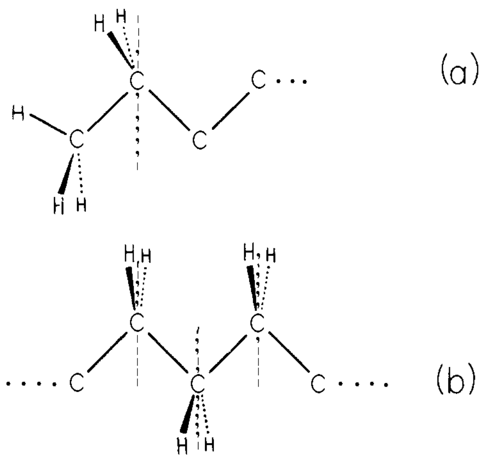

Figure 4. Influence of geminal C···H repulsive interactions upon methylene-methylene C-C bond lengths. In (a) the exterior methylene hydrogens may relax away from the plane bisecting the CCC angle, as shown, allowing the exterior methylene-methylene bond to contract. In (b) the interior methylene hydrogens in all trans segments are constrained by symmetry to lie in the plane bisecting the CCC angle and, hence, the C···H clearances are smaller and lead to longer C-C bond lengths in the interior than near the exterior of the molecule.

Table IV. Bond Lengths Calculated Using MUB-2

Bond type	Value, Å
Methyl-methyl (ethane)	1.534
Methyl-methylene (propane)	1.533
Exterior methylene-exterior methylene (*n*-butane)	1.534[a]
Exterior methylene-interior methylene (*n*-pentane)	1.535[b]
Interior methylene-interior methylene (*n*-octane, *n*-nonane)	1.537[c]

[a] Average of trans and gauche isomers assuming $\Delta G° = 550$ cal/mol. [b] Average of TT, TG, and GG isomers assuming $\Delta G° = 600$ cal/mol. [c] Average of interior TT, TG, and GG bond lengths assuming $\Delta G° = 275$ cal/mol. See text.

and $\Delta G_{g^+g^-}$, respectively) the CCC bond angle is the one differing most significantly when compared with the *n*-hexadecane, MUB-2 data set. However, a value of 114° or more for the CCC angle seems indicated for vapor-phase molecules of *n*-hexadecane and *n*-butane.[7,16] If a CCC bond angle of 114° instead of 112° had been used in the characteristic ratio calculation detailed in ref 13, the computed value would have increased to about 8.2. In any event, the difference between the two computed values is smaller than the effects of the various uncertainties in model and experiment. Similarly, the possible difference between theoretical and experimental characteristic ratios is not established precisely enough to reveal any systematic differences between the conformations of vapor-phase *n*-alkanes and condensed polymethylene.

Structure. Although the small *n*-alkane data and the *n*-hexadecane data gave approximately the same value for the characteristic ratio, there are significant differences between the structural parameters for the smaller and larger molecules. The mean bond lengths determined for *n*-hexadecane are longer than those in the short-chain *n*-alkanes studied previously. It is highly improbable that the apparent increase results from an experimental error. First, the wavelength of the diffraction beam was checked, by measurement of both the voltage and ZnO patterns. Second, as an independent check, another set of 21-cm plates was taken and analyzed after a preliminary data analysis on the first set had been completed. The new data confirmed the original results. The sample temperature was not high enough to cause by itself a significant increase in the r_g bond lengths, either by increasing the amplitude of vibration of the anharmonic oscillators ($3al^2/2$ contribution) or by increasing the concentration of gauche conformers, which presumably have longer bonds. Indeed, the *bonded* amplitudes of vibration are not markedly different from those determined for the shorter *n*-alkanes.[1,2] Some other explanation of *n*-hexadecane's long bond lengths must be sought.

The increase in the C-H bond length is of dubious significance, for the uncertainty in the value determined for the C-H bond length is fairly high, as were the uncertainties in the values determined for the C-H bond lengths of the shorter *n*-alkanes.[1,2] However, the increase in the C-C bond relative to the shorter *n*-alkanes is significant. Now, the average C-C bond in *n*-hexadecane must correspond very nearly to a methylene-methylene bond in the interior of a hydrocarbon chain, and there is some evidence that such bonds may be longer than those near the end of a hydrocarbon chain. For example, STO-3G molecular orbital calculations on ethane, propane, and gauche and *trans-n*-butane indicate that the methyl-(exterior) methylene bond is about 0.003 Å longer than the methyl-methyl bond, and that the gauche (exterior)-methylene-(exterior) methylene bond is perhaps 0.006 Å longer than the methyl-methylene bond (for trans, the difference is about 0.004 Å).[17] Calculations on ethane and propane performed with a more flexible 4-31G basis set give qualitative support to the STO-3G results; here, the difference between the (exterior) methylene-methyl and methyl-methyl C-C bonds is 0.001 Å.[17] Structural studies on cyclic alkanes indicate that the length of a methylene-methylene C-C bond may be somewhat greater than the mean C-C bond length determined for the shorter *n*-alkanes. The most recent study of cyclohexane[18] gives a C-C r_g bond length ($\pm 3\sigma$) of 1.536 ± 0.006 Å, while an electron diffraction study of cyclodecane[19] gives a length of 1.545 ± 0.002 Å. These results are equivocal apart from experimental error, for bonds in cyclohexane are free of certain nonbonded repulsions that exist in gauche sites in *n*-alkanes, and in cyclodecane the bonds around the ring depart appreciably from staggered conformations, causing effects upon the mean C-C bond length that are difficult to assess. Nevertheless, there is evidence, discussed below, that the mean length of an interior methylene bond differs from that of an exterior methylene bond.

Inferences of the effects of nonbonded repulsions were made by performing energy minimization calculations with the model force field MUB-2.[9] Since this field has reproduced experimental structural parameters quite faithfully in a series of smaller strained and unstrained hydrocarbons, it may be of some utility in analyses of differences between interior and exterior methylene-methylene C-C bonds. Table III gives the lengths of different types of C-C single bonds calculated using MUB-2. The interior methylene-methylene bond length listed was obtained by averaging the bond lengths computed for TT, TG, and GG conformations located in the middle of *n*-octane or *n*-nonane chains, assuming $\Delta G° = 275$ cal/mol. As may be seen, the interior methylene-methylene bonds are somewhat longer than the exterior methylene-methylene bonds. This variation of bond length with distance from the molecular end quickly leveled off. Part of the lengthening of C-C bonds as a function of chain length appears to be the result of the increased concentration of interior gauche bonds naturally occurring with increased chain length. Gauche bonds tend to be longer than their trans counterparts because of increased steric repulsions. However, the major portion of the bond length increase stems, according to MUB-2 results, from increased C···H geminal repulsions as the bond angles increase from their natural exterior to interior values (see Figure 4). The ultimate factor in this trend is the difference between $H-CH_2$ and

C–CH$_2$ environments. The field MUB-2 gives only an approximate account of the difference.

Other manifestations of steric interactions in *n*-hydrocarbon chains are site-to-site variations of structure parameters of the kinds postulated in previous work.[3] The most prominent of these are believed to be represented by the deformations $\Delta\phi$, ϵ, and η illustrated in Figure 5. Deformation $\Delta\phi$ increases the gauche dihedral angle from its "natural" value of 60°. The second deformation characterizes the opening up of a CCC bond angle by ϵ, or 2ϵ, when one, or both, of the C–C bonds forming the angle are involved in gauche internal rotations. The remaining parameter η represents the displacement of the trans dihedral angle from 180° induced by an adjacent gauche conformation. Presumably the deformations are additive, giving 0 for (···T[T]T···), η for (···T[T]G··), 2η for (···G$^+$[T]G$^+$···), and 0 for (···G$^+$[T]G$^-$···). The additive pattern of the postulated deformations ϵ and η was supported by later potential energy minimization calculations with the model force fields MUB-1[20] and MUB-2[9] which yielded $\Delta\phi = 2.8°$ (5.4°), $\epsilon = 1.23°$ (1.44°), and $\eta = 4.8°$ (3.1°), the MUB-2 results in parentheses. These deformations are too subtle to be isolated accurately from the statistical superposition of internuclear distances derived from the vapor-phase diffraction data. Their effects are shown in two ways, however. First, the breadths of the composite distribution peaks for internuclear distances are greater than those characteristic of individual peaks. This may be seen by comparing the experimental mean amplitudes of *n*-hexadecane in Table II with the corresponding mean amplitudes calculated for *n*-butane from vibrational frequencies. Second, the deformation parameters introduce small systematic changes in ensemble-average internuclear distances, as follows.

The displacement $\Delta\phi$ corresponding to an increase in the 3.1 Å gauche 1,3-C···C distance was determined, crudely, directly from the diffraction data to be 5 ± 10° ($\pm 3\sigma$). The other mean deformations of a long chain can be shown, as sketched previously,[3] for the 3.9 Å 1,4-(C···C)$_T$, 4.6 Å 1,5-(C···C)$_{TG}$, and 5.1 Å 1,5-(C···C)$_{TT}$ peaks, to be (angles in radians, T = 420 K, $\Delta G°$ as indicated):

$$
\begin{aligned}
(\bar{r}-r_0)_{3.9} &= -0.42\epsilon - 0.21\eta^2 && (0\ \text{cal/mol}) \\
&= -0.26\epsilon - 0.18\eta^2 && (500\ \text{cal/mol}) \\
(\bar{r}-r_0)_{4.6} &= 0.45\epsilon + 0.39\eta && (0\ \text{cal/mol}) \\
&= 0.92\epsilon + 0.39\eta && (500\ \text{cal/mol}) \\
(\bar{r}-r_0)_{5.1} &= -0.61\epsilon && (0\ \text{cal/mol}) \\
&= -0.47\epsilon && (500\ \text{cal/mol})
\end{aligned}
$$

Reference distances r_0 are assumed to be calculated from the mean values of the 1.5 Å C–C, 2.5 Å C···C, and 3.1 Å C···C internuclear distances as corrected for harmonic vibrational shrinkage effects.[21] If ϵ and η are assigned their MUB-1 or MUB-2 computed values, the 3.9 and 5.1 Å peaks are displaced inwards by about 0.01 Å while the 4.6 Å peak moves out by perhaps 0.05 Å. Now, the calculated 3.9 Å displacement is consistent with the fact, observed empirically, that in order to fit the well-defined peak it was necessary to adopt a shrinkage approximately 0.01 Å greater than that calculated for *n*-butane from spectroscopic data.[22,23] Since no vibrational shrinkage has been calculated for the weaker 4.6 Å peak and since the peak position is uncertain by several hundredths of an ångström unit, anyway, it is not possible to assign an accurate deformation displacement to the peak. There does appear to be a displacement outwards, however, as is evident in Figure 3. Therefore, it may be concluded that the experimental data are suggestive of site-to-site deformations and that the deformation magnitudes are consistent with those implicit in the model force fields. Quantitative assessments of the deformations cannot be extracted from the data, however, until detailed vibrational corrections are calculated, and even after such corrections become available, no great precision can be expected for the deformation parameters.

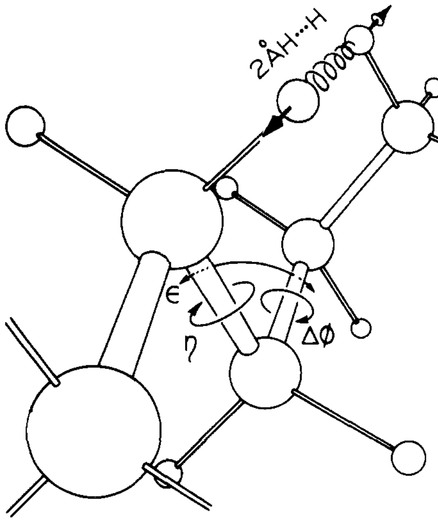

Figure 5. Identification of parameters $\Delta\phi$, ϵ, and η associated with the deformation of a trans conformation by an adjacent gauche conformation.

The greatest value of the present study is the directness with which it revealed conformational properties of free *n*-hydrocarbon chains of substantial length. Even if precise values could not be obtained for all conformational parameters of interest, certain features worthy of note were found. In particular, the major structural parameters derived differed appreciably from parameters found in studies of long hydrocarbon chains in crystals[24] and of shorter hydrocarbon chains in the vapor phase. Previous reports of CCC bond angles are more commonly in the range of 112 than 114.6°, though a recent investigation of vapor-phase *n*-butane yielded 114°.[7,10] Even more strikingly, the present long-chain C–C bond lengths exceed those in short-chain alkanes by 0.01 Å. While we were initially surprised to find this great a difference, the result is not out of line with other evidence, as discussed in the foregoing.

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Supplementary Material Available: A listing of experimental s and $I_0(s)$ values, interpolated s, $I_0(s)$, and $I_B(s)$ values, and amplitudes and shrinkage corrections for the various distances used in the analysis (16 pages). Ordering information is given on any current masthead page.

References and Notes

(1) R. A. Bonham and L. S. Bartell, *J. Am. Chem. Soc.*, **81**, 3491 (1959).
(2) R. A. Bonham, L. S. Bartell, and D. A. Kohl, *J. Am. Chem. Soc.*, **81**, 4765 (1959).
(3) L. S. Bartell and D. A. Kohl, *J. Chem. Phys.*, **39**, 3097 (1963).
(4) D. Hargittai, J. Hernadi, M. Kolonito, and G. Schultz, *Rev. Sci. Instrum.*, **42**, 546 (1971).
(5) "Tables Annuelles Internationales de Constantes", Vol. VII, Part 2, Gauthier-Villars Co., Paris, 1930, p 1795.
(6) L. S. Bartell, "Physical Methods in Chemistry", 4th ed, A. Weissberger and B. W. Rossiter, Ed., Interscience, New York, N.Y., 1972.
(7) W. F. Bradford, Ph.D. Thesis, The University of Michigan, 1975.
(8) L. Schafer, A. C. Yates, and R. A. Bonham, *J. Chem. Phys.*, **55**, 3055 (1971).

(9) S. Fitzwater and L. S. Bartell, *J. Am. Chem. Soc.*, **98,** 5107 (1976).
(10) W. F. Bradford, S. Fitzwater, and L. S. Bartell, *J. Mol. Struct.*, in press.
(11) V. Mastryukov and S. Cyvin, *J. Mol. Struct.*, **29,** 15 (1975); V. Mastryukov, private communication.
(12) L. S. Bartell and M. G. Anashkin, *J. Mol. Struct.*, **17,** 193 (1973).
(13) A. Abe, R. L. Jernigan, and P. J. Flory, *J. Am. Chem. Soc.*, **88,** 631 (1966).
(14) C. A. J. Hoeve, *J. Chem. Phys.*, **35,** 1266 (1961).
(15) R. Chiang, *J. Phys. Chem.*, **69,** 1645 (1965).
(16) S. Fitzwater, Ph.D. Thesis, The University of Michigan, 1976.
(17) W. J. Hehre, private communication.
(18) O. Bastiansen, L. Fernholt, H. M. Seip, H. Kambara, and K. Kuchitsu, *J. Mol. Struct.*, **18,** 163 (1973).
(19) R. L. Hilderbrandt, J. D. Weiser, and L. K. Montgomery, *J. Am. Chem. Soc.*, **95,** 8598 (1973).
(20) E. J. Jacob, H. B. Thompson, and L. S. Bartell, *J. Chem. Phys.*, **47,** 3736 (1967).
(21) S. J. Cyvin, "Molecular Vibrations and Mean Square Amplitudes", Elsevier, Amsterdam, 1968.
(22) The excess over the calculated butane shrinkages is 0.005 Å at 420 K or 0.013 Å at 300 K. To what extent the large vibrational amplitudes relax as the translational temperature cools during free expansion of the sample into the specimen chamber is unclear at present. The transferability of shrinkages from short to long chains is imperfect. Long-chain calculations could be performed, if warranted.
(23) J. H. Schachtschneider and R. G. Snyder, *Spectrochim. Acta*, **19,** 117 (1963).
(24) See, for example, H. M. M. Shearer and V. Vand, *Acta Crystallogr.*, **9,** 379 (1956); P. W. Teare, *ibid.*, **12,** 294 (1959); S. Abrahamsson, G. Larsson, and E. von Sydow, *ibid.*, **13,** 770 (1960); C. H. MacGillavry and M. Wolthuis-Spuy, *Acta Crystallogr., Sect. B*, **26,** 645 (1970); B. Dahlen, *ibid.*, **28,** 2555 (1972); S. Abrahamsson and B. Sunden, *ibid.*, **28,** 2562 (1972); B. Sunden, *ibid.*, **30,** 1756 (1974).
(25) NOTE ADDED IN PROOF. An experimental value of 966 ± 50 cal/mol is now available for $\Delta E°$ of *n*-butane. See A. L. Verma, W. F. Murphy, and H. J. Bernstein, *J. Chem. Phys.*, **60,** 1540 (1974). A new contribution from one- and twofold barrier components has been found to result in considerable improvements in model force fields; it enhances $\Delta E°$ per gauche link in MUB-2 by approximately 360 cal/mol according to L. S. Bartell (submitted to *J. Am. Chem. Soc.*)]

Electronic Spectra of Substituted Copper(II) Thioether Complexes

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Abstract: Electronic spectra over the 200–900-nm region are reported for mulls (80 K) and solutions (298 K) of $Cu(NH_2CH_2CH_2SCH_3)_2 \cdot 2ClO_4$, $[Cu(BuSCH_2CH_2SBu) \cdot 2X]_2$ (X = Cl, Br), $Cu(BuSCH_2CH_2SBu)_2 \cdot 2ClO_4$, $Cu(O_2CCH_2SCH_2CH_2SCH_2CO_2) \cdot H_2O$, $Cu(en)_2 \cdot 2ClO_4$, $Cu(en)_2 \cdot H_2O \cdot 2X$, and $[Cu(Me_2NCH_2CH_2NMe_2) \cdot 2X]_2$. Analyses of the ligand field and ligand to metal charge-transfer absorptions (LMCT) have been restricted to the mull spectra in order to exploit the structural information that was available from crystallographic studies. Particular attention has been devoted to the characterization of S(thioether) → Cu(II) LMCT. Identification of such absorptions in mixed ligand complexes was facilitated by characterizing the energies of N → Cu(II) and X → Cu(II) LMCT absorptions in the sulfur-free Cu(II) complexes studied. Additional indications of Cu(II)–S interactions were derived from NMR line-broadening and Raman studies. Approximately planar CuS_2N_2, CuS_2Cl_2, and CuS_4 ligand sets exhibit a strong absorption in the 22–26-μm^{-1} energy region which is assigned to $\sigma(S) \rightarrow Cu(II)$ LMCT. The observed variation in energy of this absorption may reflect the relative position of the Cu(II) d vacancy (i.e., ligand-field strength). Relative to the $\sigma(S) \rightarrow Cu(II)$ LMCT absorptions, those assignable in part to $\pi(S) \rightarrow Cu(II)$ LMCT were considerably less intense, red-shifted by ~0.5–0.7 μm^{-1}, and were not well separated in energy from interfering ligand field absorptions. Apparently LMCT absorption originating from the π orbital of thioether is considerably less intense than from the π orbitals of mercaptide.

A variety of studies have indicated that a S(cysteine)–Cu(II) chromophore is responsible for the intense coloration of the blue copper proteins.[2] As a result, the electronic structural nature of Cu(II) interactions with S donor ligands has acquired considerable research interest. Most sulfur ligands either undergo redox reactions with Cu(II) or have interfering optical spectra of their own. Simple mercaptides are instantaneously oxidized by Cu(II), while tertiary mercaptides such as $HSC(CH_3)_2CH_2NH_2$[3a] and $HSC(CH_3)_2CH(NH_2)CO_2H$[3b] react with Cu(II) to form complex $([Cu(I)]_6[Cu(II)]_6\ (ligand)_{12}Cl)$ cluster structures. Because of the availability of well characterized stable Cu(II) complexes with simple thioether ligands, they are an attractive vehicle for initiating an electronic structural investigation of Cu(II)–S bonding. This does not imply that Cu(II)–thioether complexes are appropriate bioinorganic models for the blue copper proteins, one of which (stellacyanin) does not contain any methionine residues.[4]

The study of Cu(II)–thioether bonding, until recently, largely has been restricted to solution equilibria and NMR line-broadening measurements.[5] A number of recent crystallographic studies have elucidated the structural parameters of Cu(II)–thioether bonding in a variety of complexes. These include: $Cu(Me_2NC({=}O)CH_2SCH_2C({=}O)NMe_2) \cdot 2Cl$,[6] $CuL \cdot 2ClO_4$ (L = a macrocyclic tetrathioether),[7] $Cu(NH_2CH_2CH_2SCH_3)_2 \cdot 2ClO_4$,[8] $[Cu(BuSCH_2CH_2SBu) \cdot 2Cl]_2$,[9] and $[CuL' \cdot Cl \cdot ClO_4]_2$ (L′ = 3,4-bis(2-aminoethylthio)toluene).[10] In view of this available structural information, the nature of Cu(II)–thioether bonding now may be probed by electronic-spectral measurements.

We have been able to locate only two prior electronic spectral studies of Cu(II)–thioether complexes. A recent spectral study of Cu(II) complexes with various macrocyclic polythioether ligands was not accompanied by band assignments.[7] Also presented without detailed interpretation were the spectra of Cu(II) complexes with the series of ligands $^{-}O_2CCH_2S(CH_2CH_2S)_nCH_2CO_2^{-}$ (n = 0, 1, 2).[11]

We report here the measurement and partial assignment of the electronic spectra of $Cu(NH_2CH_2CH_2SCH_3)_2 \cdot 2ClO_4$, $[Cu(BuSCH_2CH_2SBu) \cdot 2Cl]_2$, $[Cu(BuSCH_2CH_2SBu) \cdot 2Br]_2$, $Cu(BuSCH_2CH_2SBu)_2 \cdot 2ClO_4$, and $Cu(O_2CCH_2SCH_2CH_2SCH_2CO_2) \cdot H_2O$. The molecular structures of the first two complexes are known from crystallographic studies; those of the latter complexes have been established in