rather than a quadrupole parameter distribution. To test this we performed an experiment where two pulses with opposite phases and equal lengths preceded the nutation experiment. With such a rotary-echo experiment[26] the contribution to the nutation spectrum of spins with a short $T_{2\rho}$ should decrease with the length of the pulses.

For a loading of 6 water molecules per unit cell the spectra (Figure 4) show clearly a disappearing of the broad central component in the F_1 dimension. This component originates from the hydrated sodium ions at the 6-ring, since the contribution of sodium at dry 6-ring sites and hydrated 8/4-ring sites is still present (long $T_{2\rho}$) at $2\omega_{rf}$ in the F_1 dimension after pulses of 6 μs. We think that the short $T_{2\rho}$ is due to a shortening of the spin-lattice relaxation time in the rotating frame ($T_{1\rho}$) of the hydrated sodium ions at the 6-rings.

This is probably caused by an increased mobility of either the sodium ions or water molecules. In both cases the quadrupole interaction is modulated in time, causing spin-lattice relaxation. Dielectric loss and conductivity experiments[7,8] performed by Lohse et al. and Morris, respectively, suggest an increased sodium mobility with increased water content. Detailed information of this relaxation effect will be published later.

Conclusions

From the two-dimensional ^{23}Na nutation experiment we can conclude the following:

1. In dry NaA two Na sites can be detected, at the 6-rings ($e^2qQ/h = 5.8$ MHz, $\eta = 0$) and at the 8/4-rings ($e^2qQ/h = 3.2$ MHz, $\eta = 0.9$).
2. Absorption of a few molecules of H_2O per unit cell affects both sets of quadrupole parameters, but the first molecues are absorbed at the 8/4-rings.
3. After the 4 absorbed H_2O molecules the next 8 molecules are absorbed at the sodium ions at the 6-rings and have a great effect on the local symmetry around sodium, as shown by the decreased quadrupole interaction. In addition, these sodium ions have a short $T_{2\rho}$ in the rotating frame.
4. With an excess of water all sodium ions become symmetrically coordinated and all get a short $T_{2\rho}$. The short $T_{2\rho}$ is believed to be due to a modulation of the quadrupole interaction in time by either mobility of sodium ions or water molecules or both.

The two-dimensional nutation technique is very useful for the study of quadrupolar nuclei in zeolites; more information about the surroundings of the nuclei in question is obtained than with the usual one-dimensional experiment.

Acknowledgment. We thank J. W. M. van Os for his skillful technical assistance on the Bruker CXP-300. We thank Prof. Dr. E. de Boer and Dr. A. P. M. Kentgens for stimulating discussions and their interest in this work. For technical assistance at the Dutch National 500 HF NMR facility at Nijmegen (The Netherlands) we acknowledge P. A. W. van Dael and J. J. M. Joordens.

Registry No. H_2O, 7732-18-5; Na, 7440-23-5.

---

[26] Abragam, A. *Principles of Nuclear Magnetism*; Oxford University Press: London, 1961; pp 70–71.

Structure and Conformations of 1,4-Pentadiene in the Gas Phase: An Electron-Diffraction Investigation

Bruce W. McClelland[1] and Kenneth Hedberg*

Contribution from the Department of Chemistry, Oregon State University, Corvallis, Oregon 97331. *Received December 22, 1986*

Abstract: The structure and conformational composition of 1,4-pentadiene has been investigated in the gas phase at a temperature of 17 °C. With the aid of molecular mechanics calculations (MM2), three conformers of point group symmetries C_1, C_2, and C_s, which differ principally in their torsion angles about the C–C bonds, were identified as likely to be present. The best fit to our electron-diffraction data, and simultaneously to three rotational constants available for the C_1 species, is given by a mixture comprising very nearly equal amounts of each. Some of the important parameters were indicated from the MM2 calculations to have nearly identical values for each conformation and were refined as single parameters common to all forms. Values (r_g and $\angle_\alpha$) assumed to be common to the three forms with estimated 2σ uncertainties are C—C = 1.511 (2) Å, C=C = 1.339 (2) Å, C—H = 1.110 (2) Å, and $\angle$C=C—C = 125.5 (6)°. Parameter values that differ in the three forms are $\angle$C—C—C = 113.1 (11)° (C_1), 108.9 (19)° (C_2 and C_s); $\angle C_1{=}C_2{-}C_3{-}C_4 = -116.9$ (7)° (C_1), −122.2 (78)° (C_2), and −128.6 (84)° (C_s); $\angle C_2{-}C_3{-}C_4{=}C_5 = -4.3$ (69)° (C_1), −122.2 (78)° (C_2), and 128.6 (84)° (C_s). (A positive value for torsion corresponds to counterclockwise rotation of the ethylenic groups from a cis–cis C_{2v} conformation.) The C_1 form is about 0.35 kcal/mol higher in energy than the C_2 and C_s forms.

1,4-Pentadiene (hereafter PD) is the simplest hydrocarbon molecule capable of "homoconjugation", a condition that may exist when two π-systems are separated by a single methylene group.[2] The idea is that there may exist considerable overlap of the π-orbitals across this group, provided that the torsion angles around the single bonds from the separating group have the right values. In this circumstance some interesting chemistry becomes possible. An example is the di-π-methane photorearrangement[3] in which cyclization occurs by a pathway that is postulated to involve this π-orbital overlap, and that, in the case of PD, leads ultimately to the formation of vinylcyclopropane. Although this type of reaction doubtless has little direct connection with the ground-state structures of the molecules concerned, there is a question as to whether the ground-state structures are consistent with the existence of homoconjugation. For PD the matter turns largely on the values of the C=C—C—C torsion angles.

It is thought from the results of Raman[4] and microwave spectroscopy[5] that the PD molecule most probably exists in three

---

[1] Permanent address: Central Oregon Community College, Bend, Oregon 97701.

[2] See; Winstein, S. In *Carbonium Ions*; Olah, G. A., von R. Schleyer, P., Eds.; Wiley-Interscience: New York, 1972; Vol. III.

[3] See, for example: Cowan, D. O.; Drisko, R. L. *Elements of Organic Photochemistry*; Plenum: New York, 1976; Chapter 8.

[4] Gallinella, E.; Cadioli, B. *J. Chem. Soc., Faraday Trans. 2* **1975**, *71*, 781.

[5] Hirota, E., as cited in ref 4.

0002-7863/87/1509-7304$01.50/0

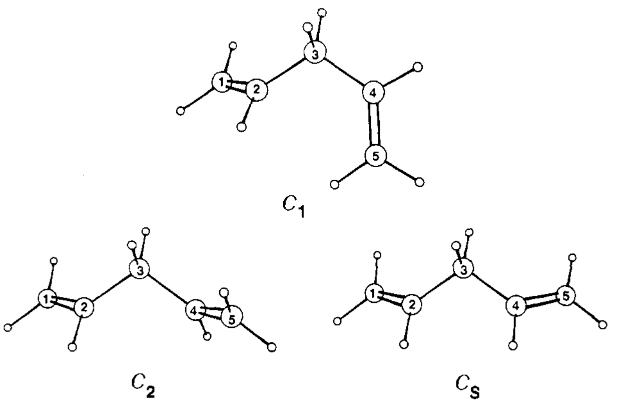


Figure 1. Conformers of 1,4-pentadiene. Relative to a hypothetical cis–cis (C_{2v} symmetry) form of the molecule, torsion around C_2–C_3 is approximately −120° in each case. Torsion around C_3–C_4 is approximately +120° for the C_s form, −120° for the C_2, and 0° for the C_1. A positive sign corresponds to counterclockwise rotation of an ethylenic group viewed from its end of the chain.

different conformations in the solid,[4] in the liquid,[4] and in the gas[5] phases. Theoretical calculations[4] led to the conclusion that the conformers have symmetries C_1, C_2, and C_s and that the C_1 form is of slightly higher energy than the others. It was later found[6] that the values of the three rotational constants, obtained in the microwave work by assignment of the spectrum of the most abundant species, could be fit only by a C_1 form. Additional theoretical calculations[6] that made use of the three rotational constants as constraints led to three, only slightly different, possible structures for the C_1 form. The shapes of these conformers of different symmetries are seen in Figure 1. They may be derived from a hypothetical, contracted, cis–cis form of the molecule (C_{2v} symmetry) to which are applied rotations of the terminal $H_2C{=}CH-$ (ethylenic) groups about their C–C single bonds. If one end of the molecule is rotated −120°, then rotation of the other end by +120°, −120°, or 0° generates respectively the C_s, C_2, and C_1 forms. (A positive rotation is counterclockwise viewed from the rotating ethylenic group toward the rest of the chain.)

There is a report[7] of the structure of PD determined by electron diffraction. In that study the PD molecule was assumed to be "non-semi-rigid", that is, the more stable conformations interconvert by virtue of large-amplitude torsions around the C–C bonds. The PD system was modeled as a mixture of pseudoconformers, each defined by values of the two torsion angles, and each weighted by a Boltzmann factor in which the steric energy calculated from molecular mechanics was used. Because of its basis in the results of molecular mechanics, this model does not address the interesting question of the values of the torsion angles directly. As it turns out, we had undertaken, but not completed, a concurrent study of PD based on a model of the system comprising a mixture of well-characterized conformers such as those described in the preceding paragraph. Our objectives had been to establish the identity of the conformers, if possible to evaluate their relative stabilities, and to measure the values of the torsion angles which are the most important of the parameters that distinguish the conformers. Our study is now finished, and because our final results differ in some important respects from those previously published, we feel it worthwhile to present them.

Experimental Section

The sample of 1,4-pentadiene (99%) was obtained from Aldrich Chemical Co. and was used without further purification.

Diffraction photographs were made in the Oregon State apparatus with use of an r^3 sector. Experimental conditions for the diffraction experiment were as follows: average sample bath temperature, −58 °C; nozzle-tip temperature, 16–18 °C; ambient apparatus pressure during exposures, 4.8–9.3 × 10^{-6} Torr; nominal electron wavelength, 0.057 Å (calibrated in separate experiments with CO_2: $r_a(C{=}O) = 1.1646$ Å, $r_a(O{\cdot}O) = 2.3244$ Å); nominal camera distances, 750 mm (long) and 300 mm (middle); photographic plates, 8 × 10 in Kodak projector slide medium contrast; exposure times, 60–210 s; development, 10 min in D-19 developer diluted 1:1; data ranges, $2.00 \leq s/\text{Å}^{-1} \leq 12.75$ (long), $7.00 \leq s/\text{Å}^{-1} \leq 32.25$ (middle); data interval, $\Delta s = 0.25$ Å^{-1}. Procedures for obtaining the total scattered intensities ($s^4I_t(s)$), backgrounds, and molecular intensities ($sI_m(s)$) have been described.[8,9] The total intensity curves, backgrounds, and average molecular intensity curves are shown in Figure 2 and are available as supplementary material.

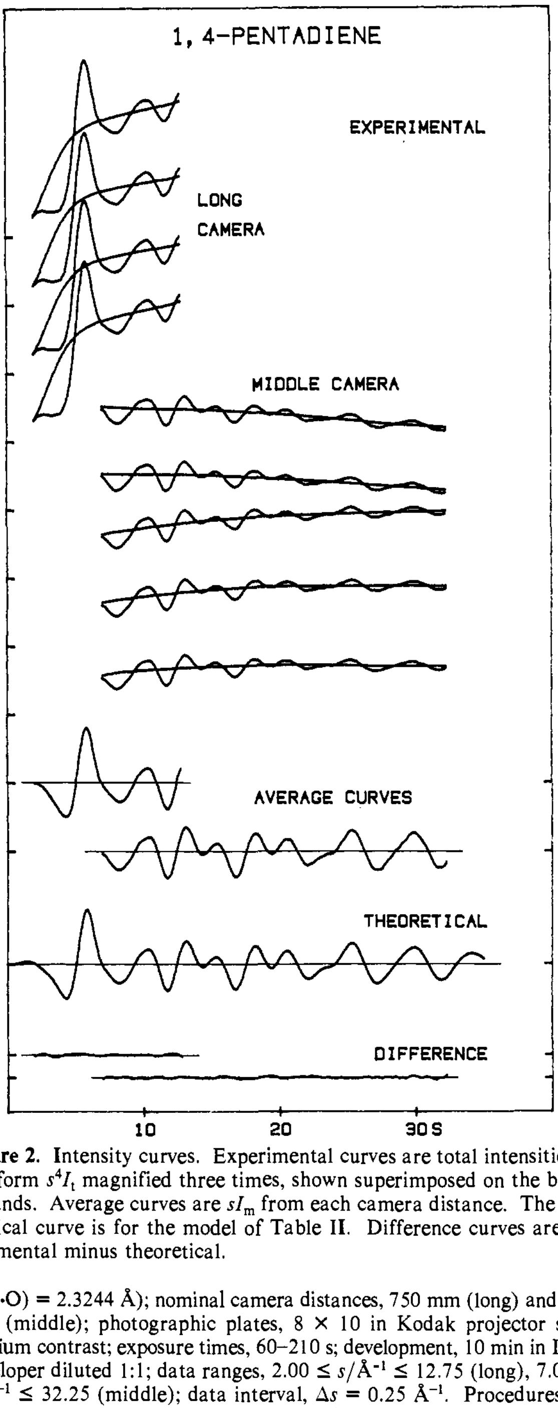


Figure 2. Intensity curves. Experimental curves are total intensities in the form s^4I_t magnified three times, shown superimposed on the backgrounds. Average curves are sI_m from each camera distance. The theoretical curve is for the model of Table II. Difference curves are experimental minus theoretical.

Radial distribution curves were calculated from a composite of the average molecular intensities multiplied by $Z_C{}^2F_C{}^{-2}[\exp(-0.0025s^2)]$, using theoretical data in the unobserved or uncertain region $0 \leq s/\text{Å}^{-1} \leq 2.75$. Figure 3 shows the final experimental curve.

Electron scattering amplitudes and phases for all calculations were interpolated from tables.[10]

Structural Analysis

The features of the radial distribution curve below about 2.7 Å were easily interpreted in terms of those portions of the PD

---

(6) Cadioli, B.; Gallinella, E. *J. Mol. Struct.* **1976**, *31*, 199.

(7) Ter Brake, J. H. M. *J. Mol. Struct.* **1984**, *118*, 73.

(8) Gundersen, G.; Hedberg, K. *J. Chem. Phys.* **1969**, *51*, 2500.

(9) Hedberg, L. Abstracts, Fifth Austin Symposium on Gas-Phase Molecular Structure, Austin, TX, 1974; No. T9.

(10) Elastic amplitudes and phases: Schafer, L.; Yates, A. C.; Bonham, R. A. *J. Chem. Phys.* **1971**, *56*, 3056. Inelastic amplitudes: Cromer, D. T. *Ibid.* **1969**, *50*, 4857.

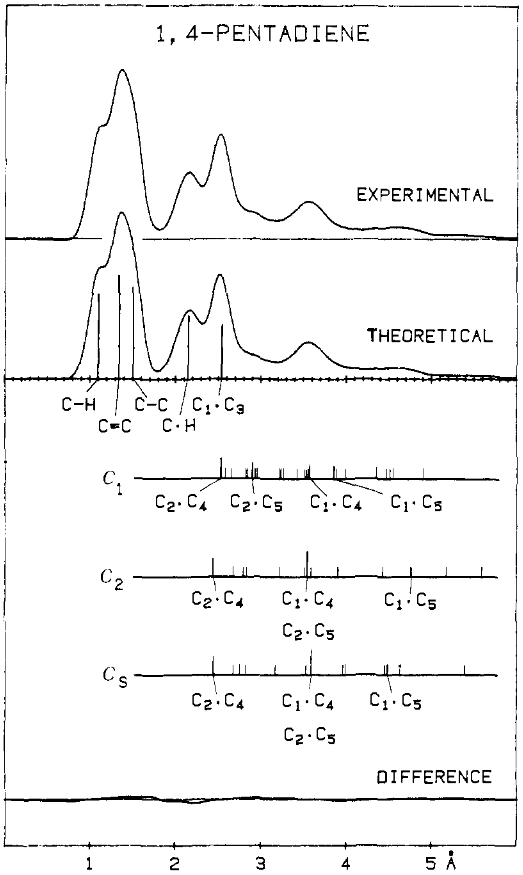


Figure 3. Radial distribution curves. The theoretical curve is for the model of Table II. Weights and locations of terms common to all conformers are shown by the set of longer vertical bars. Locations of conformer-dependent C··C and C··H terms are shown below; the weights of the C··C terms relative to those for the longer set have been doubled for clarity; the lengths (weights) of the C··H terms are arbitrary.

molecule that would be expected to have the same, or nearly the same, structure regardless of molecular conformation. The parameters describing those aspects of the system were taken to be the bond lengths C—C, C=C, and C—H, the bond angles C—C—C and C=C—C, the weighted average H—C—H bond angle $\langle\angle\text{H-C-H}\rangle$ (equal to $[2\angle\text{H-C}_{\text{trig}}\text{-H} + \angle\text{H-C}_{\text{tetra}}\text{-H}]/3$), and the angle difference $\Delta\angle\text{H-C-H}$ (equal to $\angle\text{H-C}_{\text{trig}}\text{-H} - \angle\text{H-C}_{\text{tetra}}\text{-H}$). The hydrogen atoms in the C=CH—C groups were positioned such that the C=C—H and C—C—H angles were always equal, an assumption consistent with the results of molecular mechanics calculations. Local C_{2v} symmetry was assumed for all $\text{-CH}_2\text{-}$ groups. The details of the radial distribution curve beyond 2.7 Å were not so readily interpreted because they depend on structural features that differ among the conformers and, should more than one conformer be present, on the relative amount of each. The parameters chosen to represent these aspects of the system were the torsion angles $C_1{=}C_2{-}C_3{-}C_4$ and $C_2{-}C_3{-}C_4{=}C_5$ associated with the C-C bonds in each conformer and the mole fractions of two of the three conformers.

Several models (described below) of the system were developed that provided approximate fits to the experimental radial distribution curve in the conformer-sensitive region. These models were refined by least-squares adjustment[11] of the corresponding theoretical intensity curves to the two average experimental curves or by a similar adjustment in which the three theoretical rotational constants for the C_1 conformer were included in the experimental data. Contributions from all atomic pairs were included. A unit weight matrix was assigned to the diffraction data, and the rotational constants, when included, were weighted such that the sum of the weighted squares of the values was about 650 times greater than the sum of the weighted squares of the electron-diffraction intensities.

Table I. Parameter Values and Steric Energies of 1,4-Pentadiene from Molecular Mechanics[a]

	conformer		
	C_1	C_2	C_s
distances (Å)			
$r(C_2{-}C_3)$	1.510	1.508	1.508
$r(C_3{-}C_4)$	1.511	1.508	1.508
$r(C_1{=}C_2)$	1.341	1.341	1.341
$r(C_4{=}C_5)$	1.341	1.341	1.341
$\langle r(\text{C—H})\rangle^b$	1.106	1.106	1.106
angles (deg)			
$\angle(\text{C—C—C})$	115.2	110.6	110.7
$\angle(C_1{=}C_2{-}C_3)$	123.9	123.9	123.9
$\angle(C_3{-}C_4{=}C_5)$	125.2	123.9	123.9
$\angle(C_1{=}C_2{-}C_3{-}C_4)$	−115.0	-117.5^c	-118.3^d
$\angle(C_2{-}C_3{-}C_4{=}C_5)$	11.1	-118.3^c	117.8^d
energy, E_s (kJ·mol^{-1})	12.23	8.385	8.682
percent[e]	17.8	43.7	38.6

[a] MM2. [b] Average of all C—H bonds. [c,d] The inequality of these numbers is because no symmetry condition was imposed in the calculation. [e] Composition calculated from Boltzmann distribution based on steric energies.

Since it was necessary to specify the model in terms of the $r_\alpha{}^0 = r_z$ type of distance when rotational constants for the C_1 conformer were to be included in the refinements, we found it convenient to use this distance type for the other conformers as well. The corrections of B_0 to B_z and $r_\alpha{}^0$ to r_a, required for the scattered intensity calculation, were calculated[12] from a rough quadratic vibrational force field based on C_{2v} symmetry for a model of PD with bond distances and bond angles similar to our final ones. The force field was used for all conformers; it reproduced the observed[4] fundamental frequencies to within 15 cm^{-1}. The observed[5] values of the rotational constants are A_0 = 11064.17 MHz, B_0 = 3154.62 MHz, and C_0 = 2683.38 MHz, and our converted values are A_z = 11071.47 MHz, B_z = 3151.46 MHz, and C_z = 2682.28 MHz. Theoretical rotational constants were calculated with the conversion factor B_zI_z = 505379 MHz·u·Å^2.

We first tested models in which only one conformer, C_1, C_2, or C_s, was assumed to be present. Trial values for the parameters of these structures were obtained from molecular mechanics calculations (MM2[13]); they are seen in Table I. The large number of vibrational parameters required to specify completely a particular model was kept at a reasonable level by giving some nonbond amplitudes values calculated from the force field mentioned above and then refining them in groups. All H·H amplitudes were held at averages of values calculated for terms of similar types. As expected, the results for corresponding bond distances and bond angles were the same for the molecules of each symmetry to within the experimental uncertainties. Of some surprise, however, was the result that with suitable adjustment of the torsion angles, each of these conformations could be made to fit *all* the diffraction data tolerably well, and one model for the C_1 conformer was found that fit them quite well. Some aspects of this C_1 model were troublesome, however. Values of the rotational constants calculated for it were unacceptably different from those observed. Further, the model had an unacceptably small nonbond torsion-sensitive H·H distance, $\text{H}_{\text{C2}}\cdots\text{H}_{\text{C5}}$. The main source of these difficulties seemed to be a too small value (108.6 (15)°) for the apical angle, ∠C-C-C, which is predicted from the MM2 calculations to be substantially larger in the C_1 conformer than in the C_2 or C_s conformer. When the observed rotational constants were included in the refinement, the apical angle obtained a larger value, 112.7 (14)°. However, the quality of fit of the C_1 model to the electron-diffraction data deteriorated somewhat to about that provided by the C_2 and C_s models. Thus, as has been observed before in this laboratory,[14] a molecular model

---

(11) Hedberg, K.; Iwasaki, M. *Acta crystallogr.* **1964**, *17*, 529.

(12) Hedberg, L. Abstracts, Seventh Austin Symposium on Gas-Phase Molecular Structure, Austin, TX 1978; p 49.

(13) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127.

Table II. Selected Parameter Values for 1,4-Pentadiene

	parameter values common to all conformers					
	this work^a					ref 7^b
	r_α°, $\angle_\alpha$	r_g	r_a	l_{obsd}	l_{calcd}	r_α, $\angle_\alpha$
C—C (Å)^c	1.508 (2)	1.511	1.509	0.062 (3)	0.052	1.505 (1)
C=C (Å)^c	1.334 (2)	1.339	1.336	0.054 (2)	0.043	1.336 (1)
C—H (Å)^c	1.090 (2)	1.110	1.104			1.074 (2)
∠(C=C—C) (deg)^c	125.5 (6)					125 (1)
∠(C_2=C_1—H) (deg)^d	123.2 (9)					126 (2)
∠(C_1=C_2—H) (deg)^e	117.3 (3)					114 (2)
∠(C_2—C_3—H) (deg)^d	109.7 (6)					110 (2)
R^e	0.051					

	parameter values for conformers of different symmetries					
	this work^f			ref 7^{f,g}		
	C_1	C_2	C_s	C_1	C_2	C_s
∠(C—C—C) (deg)	113.1 (11)	108.9 (19)^h	108.9 (19)^h	113 (1)^i	113 (1)^i	113 (1)^i
∠(C_1=C_2—C_3—C_4) (deg)	-116.9 (7)	-122.2 (78)	-128.6 (84)	-115	-120	-120
∠(C_2—C_3—C_4=C_5) (deg)	-4.3 (69)	-122.2 (78)	128.6 (84)	-5	-120	120
X^j	0.35 (19)	0.33 (29)	0.32 (29)	22^k	39^k	40^k

[a] Quantities in parentheses are estimated 2σ. [b] Quantities in parentheses are 1σ. [c] Assumed to be independent of conformation. [d] Dependent parameter in our model. Independent parameter values were ⟨∠(H—C—H)⟩ = 110.7 (19)° and Δ∠(H—C—H) = 9.0° (assumed). See text for definitions. [e] $R = [\sum_i w_i \Delta_i^2 / \sum_i w_i (s_i I_i(\text{obsd}))^2]^{1/2}$ where $\Delta_i = s_i I_i(\text{obsd}) - s_i I_i(\text{calcd})$. [f] Torsion angles are with reference to zero values for a cis–cis (C_{2v}) form of the molecule. [g] Torsion angles are for the three conformers corresponding to minima in the torsional potential. [h] Refined as a group. [i] Assumed to be the same for all forms. [j] Mole fraction. [k] Values calculated by us from authors's data for these three conformers.

Table III. Interatomic Distances (r/Å) and Vibrational Amplitudes (l/Å) for Conformers of 1,4-Pentadiene^a

	C_1			C_2			C_s		
	r_g	l_{obsd}	l_{calcd}	r_g	l_{obsd}	l_{calcd}	r_g	l_{obsd}	l_{calcd}
$C_1 \cdot C_3$	2.530 (7)	0.070 } (5)	0.065	2.531 (7)	0.069 } (5)	0.065	2.530 (7)	0.069 } (5)	0.065
$C_2 \cdot C_4$	2.520 (17)	0.082	0.077	2.456 (29)	0.082	0.077	3.582 (45)	0.069	0.065
$C_1 \cdot\cdot C_4$	3.570 (14)	0.155 } (16)	0.115	3.543 (45)	0.157 } (16)	0.117	3.582 (46)	0.153 } (16)	0.113
$C_2 \cdot\cdot C_5$	2.896 (13)	0.159	0.119	3.543 (45)	0.157	0.117	3.582 (46)	0.113	0.113
$C_1 \cdot\cdot C_5$	3.872 (17)	0.188 (73)	0.188	4.756 (66)	0.120 (73)	0.120	4.499 (138)	0.190 (73)	0.190
$C_1 \cdot H_{C2}$	2.090 (5)	0.103 } (6)	0.098	2.090 (5)	0.104 } (6)	0.098	2.089 (5)	0.104 } (6)	0.098
$C_2 \cdot H_{C1}$	2.149 (9)	0.105	0.100	2.149 (9)	0.105	0.099	2.149 (9)	0.105	0.099
$C_2 \cdot H_{C3}$	2.148 (8)	0.121	0.116	2.161 (6)	0.121	0.116	2.162 (6)	0.121	0.116
$C_3 \cdot H_{C2}$	2.242 (5)	0.107	0.102	2.240 (5)	0.107	0.102	2.242 (5)	0.107	0.102

[a] Quantities in parentheses are estimated 2σ uncertainties. Quantities in brackets were refined as groups.

found to give a very good fit to the diffraction data was found to be incompatible with observed rotational constants. One other feature of the C_1 conformer was explored in these test refinements of single conformers. The MM2 calculations predict somewhat different values for the two C=C—C bond angles in the C_1 conformer, and accordingly an average and a difference parameter for these angles was introduced. A typical refinement result for the angle difference, based on simultaneous fits to the diffraction data and the rotational constants, was 0.4 (49)°. We concluded that for our work the difference was not detectably different from zero, and in all subsequent refinements the values of the two C=C—C angles were assumed to be equal.

Although separate models for each conformer could be made to fit the data tolerably well, the fits were not quite as good as those we have come to expect for molecules having only atoms of low atomic number. Judged from this past experience, our data for PD are quite consistent with the spectroscopic evidence, and with the results of the MM2 calculations, which clearly show the PD system to comprise a mixture of conformers. In order to model such a system, which is much more complicated that the single molecule systems described above, a number of simplifying assumptions in addition to those already described for the single conformer models were necessary. Among these (supported by our results from refinements of the single conformer models and by the MM2 calculations) was the equality of the lengths of all corresponding bonds and of the values of most of the corresponding bond angles, in the three conformers. An exception was the apical C–C–C angle in the C_1 conformer which, for reasons mentioned above, was expected to be larger than in the other species. Except for the apical angle, treated as a separate parameter in the C_1 from that in the C_2 and C_s species, and for the torsion angles of each of the conformers that were of course treated independently, the set of geometrical parameters was as in the refinements of the single conformers. Corresponding amplitudes (or groups of amplitudes) between conformers were refined as groups. Initially, the amounts of each conformer were fixed at mole fractions determined from the MM2 strain energies (Table I) with the assumption of a Boltzmann distribution. Later, the composition parameters (mole fractions) were allowed to refine. The poorly determined parameter Δ∠H–C–H was fixed at 9.0° after attempts to refine it resulted in unreasonable values. The final model, which provides a very good fit to both the electron-diffraction data and the rotational constants, is presented in Tables II and III and the correlation matrix for the refined parameters is given in Table IV. The theoretical intensity curve calculated from the model is shown in Figure 2 and the corresponding radial distribution curve in Figure 3.

Discussion

There is nothing about the ground-state molecular structure of PD that would suggest facile di-π-methane rearrangement. As is seen from Table V, the parameter values of PD and 1-butene,[15,16] the latter a molecule that cannot undergo the rearrangement, are essentially the same. Further, in each form of both molecules a C=C bond approximately eclipses either a methylene C–H or a C–C bond. There are some small differences between the structures of the two molecules, the most interesting of which are the values of the C–C–C angles: in both forms of 1-butene they

---

(14) Hedberg, L.; Hedberg, K. *J. Phys. Chem.* **1982**, *86*, 598.

(15) Iijima, T. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1291.

(16) Van Hemelrijk, D.; Van den Enden, L.; Geise, H.; Sellers, H.; Schafer, L. *J. Am. Chem. Soc.* **1980**, *102*, 2189.

Table IV. Correlation Matrix for Parameters of 1,4-Pentadiene

	$\sigma_{LS}{}^a \times 100$	r_1	r_2	r_3	$\angle_4$	$\angle_5$	$\angle_6$	$\langle\angle\rangle_7$	$\Delta\angle_8$	τ_9	τ_{10}	τ_{11}	τ_{12}	l_{13}	l_{14}	l_{15}	l_{16}	l_{17}	l_{18}	X_{19}	X_{20}
1. r(C—C)	0.059	100	54	15	10	−31	−41	47	−34	−47	35	−9	11	−1	39	35	0	−1	−2	20	8
2. r(C=C)	0.046		100	37	6	−15	−36	38	−17	−35	20	3	3	−36	−2	34	−2	−4	−9	14	−12
3. r(C—H)	0.075			100	−2	7	−13	26	1	−14	2	4	3	−29	−23	5	3	−7	2	−3	6
4. ∠C—C—C: C_1	39				100	−8	−80	40	2	−5	70	−7	4	1	5	−1	30	−16	−5	49	−11
5. ∠C—C—C: C_2, C_s	73					100	−14	−66	41	32	−40	44	23	−13	−28	−11	72	−13	4	−36	17
6. ∠C=C—C	21						100	−16	−2	17	−53	−7	−14	9	−10	−15	−54	16	5	−53	9
7 ⟨∠H—C—H⟩^{b}	72							100	−41	−39	65	−25	−2	−6	15	14	−37	0	−4	16	0
8 Δ∠H—C—H^b	741								100	88	−67	3	−36	−3	−25	−19	11	−33	−7	−5	−27
9. $\tau_{23}{}^c$:C_1	54									100	−72	0	−36	5	−23	−25	1	−25	−5	−12	−23
10. $\tau_{34}{}^c$:C_1	325										100	−9	25	1	21	13	8	10	1	37	10
11. $\tau_{23} = \tau_{34}$:C_2	272											100	−18	−6	−9	0	36	−7	3	−15	−20
12. $\tau_{23} = -\tau_{34}$:C_s	311												100	−3	6	4	32	0	−31	−5	29
13. l(C—C)	0.047													100	50	−1	−2	7	−1	9	−5
14. l(C=C)	0.040														100	15	−1	9	−4	19	−3
15. l(C—H)	0.061															100	3	6	0	8	0
16. l(C_1·C_3)	0.15																100	−16	2	13	11
17. l(C_1··C_4)	0.56																	100	22	−22	3
18. l(C_1···C_5)	2.5																		100	−10	46
19. $X(C_1)^d$	6.7																			100	−33
20. $X(C_2)^d$	11																				100

[a] Distances (r) and amplitudes (l) in angstroms, angles in degrees. [b] See text for definition. [c] τ_{23} = ∠C_1=C_2—C_3—C_4; τ_{34} = ∠C_2—C_3—C_4=C_5. [d] Mole fractions.

Table V. Parameter Values for Comparable Forms of 1,4-Pentadiene and 1-Butene

	C_1 (PD); or syn (1-Bu)			C_2 and C_s (PD); or skew (1-Bu)		
		1-butene			1-butene	
	1,4-PD^a	ED^b	MW^c	1,4-PD^a	ED^b	MW^c
r(C—C) (Å)	1.511 (2)	1.502 (2)^d	1.507 (10)	1.511 (2)	1.502 (2)^d	1.493 (8)
r(C=C) (Å)	1.339 (2)	1.340 (4)	1.336 (8)	1.339 (2)	1.340 (4)	1.342 (9)
∠C—C—C (deg)	113.1 (11)	114.9 (3)^e	114.8 (5)	108.9 (19)	111.7 (3)^e	112.1 (2)
∠C=C—C (deg)	125.5 (6)	127.2 (3)^e	126.7 (4)	125.5 (6)	125.6 (3)^e	125.4 (2)
∠C—C—C=C (deg)	−4.3 (69)	[0.0]	[0.0]	−122.2 (78) (C_2) 128.6 (84) (C_s)	−119.9 (3)	−119.9 (3)

[a] This work; r_g distances. [b] Reference 16; r_g distances. [c] Reference 17; r_0-like structure. [d] C_2—C_3. [e] Differences between syn and skew forms taken from ab initio calculations.

exceed slightly those in the comparable forms of PD. It seems likely that these angle differences are due to steric repulsions that are greater between the methyl and ethylenic groups in 1-butene than they are between the two ethylenic groups in PD. Torsion around the two single bonds in PD allows the hydrogen atoms of the two =CH— groups to avoid each other in a way denied to the hydrogen atoms of the =CH— and CH_3 groups of 1-butene. In the C_2 and C_s forms of PD particularly, the ethylenic groups appear to interact very little, leading to an essentially tetrahedral C-C-C angle. In the C_1 form the interaction is greater and the C-C-C angle corresponding increased, as it is in propane (112.0°[17]) with two interacting methyl groups. The greater interaction in the C_1 form is also reflected in the relative magnitudes of ∠C_1=C_2—C_3—C_4 in the three conformers; this angle is largest in the C_1 form as the ethylenic group rotates further to minimize repulsion.

A comparison of Tables I and II offers further evidence that there are no abnormalities in the structure of PD. The bond lengths and bond angles are in good agreement with those predicted from molecular mechanics. So also are the values of both torsion angles for the C_2 and C_s conformers, and of ∠C_1=C_2—C_3—C_4 for the C_1 conformer, when the rather large experimental uncertainties are taken into account. The experimental value for ∠C_2—C_3—C_4=C_5 in the C_1 conformer differs appreciably from the calculated one, but we do not regard the difference to be important because the C_1 steric energies from MM2 are quite insensitive to small changes in the torsion angles in the region of the potential minimum.

The relative amount of each of the three conformers in the gas phase is of special interest. Our molecular mechanics calculations indicated that the C_1 conformer should be present in the smallest amount, but the microwave work[5] indicated that it should be the dominant species. Unfortunately, the uncertainties attached to our results for the composition do not allow us to settle the question. Beyond this, we may use our results for the conformational composition for a crude estimate of the energy differences between the conformers. With the assumption of no difference in the vibrational and rotational entropies, but with allowance for the existence of enantiomers in the ratio 2:1:1 for the forms C_1:C_2:C_s, these energy differences in kcal/mol are $E^0(C_1) - E^0(C_2)$ = 0.37 (13), $E^0(C_1) - E^0(C_s)$ = 0.35 (13), and $E^0(C_s) - E^0(C_2)$ = 0.02 (17). The values are consistent with the Raman work on PD[2] which indicates that the three conformers have nearly the same energies. Further, the energy differences for the C_1,C_2 and C_1,C_s pairs of PD are similar to the difference between the syn and skew forms of 1-butene (0.53 (42) kcal/mol by electron diffraction,[16] 0.15 (15) kcal/mol by microwave spectroscopy,[17] and about 0.2 kcal/mol estimated from infrared intensities[18]), a fact consistent with the other parallels mentioned above.

We have noted that the structure of PD has been investigated previously[7] with use of a model comprising a system of pseudoconformers, each weighted by a Boltzmann factor determined by a steric energy for the pseudoconformer calculated from molecular mechanics. This scheme removed the torsion angles from the list of parameters accessible to refinement and reduced the structural problem to that of a determination of the average bond distances and average bond angles only. The results are summarized in Table II, and for the most part they are seen to be in very good agreement with ours. Due to the nature of the earlier author's model, however, the more subtle aspects of the structures of the conformers, such as differences in the values of ∠C–C–C and the

---

(17) Kondo, S.; Hirota, E.; Morino, Y. *J. Mol. Spectrosc.* **1968**, *28*, 471.

(18) Barnes, A.; Howells, J. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 532.

J. Am. Chem. Soc. 1987, 109, 7309-7314

torsion angles, were not investigated.

Acknowledgment. We are indebted to the National Science Foundation which supported this work under Grants CHE81-10541 and CHE84-11165. B.W.M. is grateful to Central Oregon Community College for a summer stipend. Thanks are due Peter K. Freeman for helpful discussions about homoconjugation in PD and to Lise Hedberg for helpful discussions concerning the vibrational force field.

Supplementary Material Available: Tables of total scattered intensities, calculated backgrounds for each plate, and averaged molecular intensities (11 pages). Ordering information is given on any current masthead page.

Photochemical Hydrogen Evolution via Singlet-State Electron-Transfer Quenching of Zinc Tetra(*N*-methyl-4-pyridyl)porphyrin Cations in a Zeolite L Based System

Lalchan Persaud, Allen J. Bard, Alan Campion, Marye Anne Fox, Thomas E. Mallouk,* Stephen E. Webber, and J. M. White

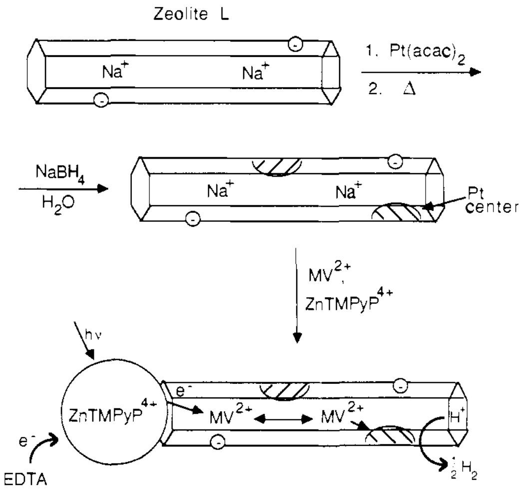
Contribution from the Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712. *Received December 23, 1986*

Abstract: Molecular electron transport chains composed of EDTA, zinc tetra(*N*-methyl-4-pyridyl)porphyrin ($ZnTMPyP^{4+}$), and methylviologen (MV^{2+}), spatially organized by 1 μm diameter zeolite L particles, were studied. MV^{2+} ion exchanges into zeolite L to a maximum loading of $2.5–3.0 \times 10^{-4}$ mol/g of zeolite, while the bulkier $ZnTMPyP^{4+}$ adsorbs only onto the outer surface in approximately monolayer (8×10^{-6} mol/g) quantities. At pH 4.0, $EDTA^{2-}$ is strongly adsorbed onto the $ZnTMPy^{4+}$-coated surface. When the composite is prepared from internally platinized zeolite L particles, hydrogen is evolved photochemically from water in pH 4.0, 2×10^{-3} M EDTA solution. The rate of hydrogen evolution depends on the MV^{2+} loading, no H_2 being evolved below 1.5×10^{-4} mol MV^{2+}/g (ca. 0.4 MV^{2+} ion per large cavity). $ZnTMPyP^{4+}$ shows a biphasic fluorescence decay when adsorbed on the zeolite L surface. The rapidly decaying component has a lifetime varying from <20 ps to 150 ps; the inverse lifetime (fluorescence decay rate) shows the same dependence on MV^{2+} loading as the hydrogen evolution rate. The slowly decaying fluorescence component and the time-resolved triplet–triplet absorbance are invariant with MV^{2+} loading. These observations are explained in terms of singlet-state electron-transfer quenching of $ZnTMPyP^{4+}$ by MV^{2+}. The triplet excited state reactivity of $ZnTMPyP^{4+}$ is suppressed by a 200-mV positive shift of its redox potentials caused by adsorption onto the zeolite surface.

The study and development of molecular systems for light-to-chemical energy conversion are of both fundamental and practical importance. Among the best-studied artificial photosynthetic systems are homogeneous and heterogeneous (micelles, vesicles, etc.) fluids which employ a sensitizer, such as a polypyridyl–ruthenium complex or porphyrin, in conjunction with an electron relay (quencher) and a sacrificial electron donor or acceptor.[1] The excited state of the sensitizer must be sufficiently long-lived so that electron transfer to or from the quencher may occur on a diffusional time scale, i.e., in several nanoseconds or more. Thus, while metalloporphyrins have photophysical properties which make them desirable as sensitizers, in homogeneous solution their excited singlet states are not sufficiently long-lived for electron-transfer quenching.[2] In microstructurally organized media, singlet-state quenching of porphyrins and similar molecules may occur; for example, in the reaction center of *rhodopseudomonas viridis*,[3] close juxtaposition of macrocyclic light absorbers and quenchers allows efficient electron-transfer quenching on a time scale of a few picoseconds.[4] In special situations, man-made systems, in which the porphyrin is tethered covalently to an electron acceptor, show rapid singlet-state electron-transfer quenching.[5] The synthesis of these molecules is generally quite challenging, however, and the formation of chemical products from the singlet-state reaction has been demonstrated only once.[6]

In this paper we describe a metalloporphyrin-based electron-transport chain which self-assembles by virtue of ion exchange and steric interactions with a zeolite L particle. The microstructure imposed by the zeolite permits zinc tetra(*N*-methyl-4-pyridyl)porphyrin, $ZnTMPyP^{4+}$, to be held in sufficient proximity to a methylviologen (MV^{2+}) cation so that singlet-state electron-transfer quenching occurs on a subnanosecond time scale. With

Scheme I



---

* Author to whom correspondence should be addressed.

(1) (a) Kalyanasundaram, K.; Graetzel, M. *Helv. Chim. Acta* **1980**, *63*, 478. (b) Lehn, J. M.; Sauvage, J. P.; Ziessel, R. *Nouv. J. Chim.* **1980**, *4*, 355. (c) Johansen, O.; Mau, A. W. H.; Sasse, W. H. F. *Chem. Phys. Lett.* **1983**, *94*, 107. (d) Harriman, A.; Porter, G.; Richoux, M. C. *J. Chem. Soc., Faraday Trans. 2* **1981**, *77*, 883. (e) Harriman, A.; Porter, G.; Wilowska, A. *J. Chem. Soc., Faraday Trans. 2* **1984**, *80*, 191. (f) Blondell, G.; DeKeukeleire, D.; Harriman, A.; Milgrom, L. R. *Chem. Phys. Lett.* **1985**, *118*, 77. (g) Shafirovich, V. Y.; Khannov, N. K.; Strelets, V. V. *Nouv. J. Chim.* **1980**, *4*, 81. (h) Fitzpatrick, L.; Goodwin, H. A.; Launikonis, A.; Mau, A. W. H.; Sasse, W. H. F. *Aust. J. Chem.* **1983**, *36*, 2169.

0002-7863/87/1509-7309$01.50/0