by Masamune.[7,8] The range of C=C bond distances in **4** is extremely narrow with the five values being 1.332, 1.333 (two), and 1.334 Å (two). A slightly larger spectrum of C–C distances is predicted, namely 1.519, 1.510 (two), and 1.500 Å (two), with all five lying within the normal range of carbon–carbon single bonds. This isomer is seen to be even more effective than the all-cis form (**3**) in reducing the 144° CCC bond angles required by the D_{10h} aromatic structure. The largest CCC bond angle in **4** is 130.0° while the smallest is 121.0°. In this structure, the C_{10}-$C_1C_2C_3$ dihedral angle is found to be 155.1°, significantly different from the 180° for an ideal trans configuration. **4** is predicted to lie 9 kJ mol^{-1} (4-31G//STO-2G) below **3**.

***TCTCC* [10]Annulenes (5 and 6).** Optimized geometries have been obtained for two conformations (**5** and **6**) of the *TCTCC* isomer of [10]annulene (Figure 5). The lower energy form is **5** with C_2 symmetry and a twofold axis bisecting the $C_1{=}C_2$ and $C_6{-}C_7$ bonds. As for the previous isomers **3** and **4**, the name 1,3,5,7,9-cyclodecapentaene is very appropriate. The double bond lengths are 1.339 (two), 1.334 (two), and 1.337 Å, while the single bonds are of lengths 1.512, 1.498 (two), and 1.508 Å (two). None of the CCC angles is particularly strained with the five independent angles falling between 122.9° and 130.3°. The $C_1C_{10}C_9C_8$ and $C_2C_3C_4C_5$ dihedral angles are −153.2°, again significantly distorted from 180°. The predicted structure of **5** contrasts with that determined experimentally[41] for crystals of a derivative of Vogel's methano-bridged system (**13**). Whereas the carbon ring in the methano-bridged system is very similar to that of **5** in being almost planar, the range of CC bond lengths in **13** is only 1.38–1.42 Å, i.e., there is no longer a separation into single and double bonds.

5 is predicted to lie only 12 kJ mol^{-1} (4-31G//STO-2G) above the *TCCCC* isomer **4**. Thus we would predict that **5** may well be an observable isomer of [10]annulene.

The second conformation (**6**) of the *TCTCC* isomer was optimized under a C_s symmetry constraint with the plane of symmetry bisecting the bonds $C_1{=}C_2$ and $C_6{-}C_7$. Strong alternation of bond lengths is again evident. **6** lies 36 kJ mol^{-1} above **5** or 48 kJ mol^{-1} above **4**. As with **5**, the $C_8C_9C_{10}C_1$ and $C_5C_4C_3C_2$ dihedral angles are noticeably different from 180°, namely ±155.2°.

Concluding Remarks

The structures and energies of the [10]annulenes predicted here from ab initio molecular quantum mechanical calculations are for the most part consistent with the picture obtained indirectly from experiment by Masamune and co-workers.[7,8,12,13] The two structures **3** (all-cis) and **4** (*TCCCC*) observed by Masamune are indeed those predicted by the theory to lie lowest in energy. A third low-energy isomer **5** (*TCTCC*), lying just 3 kJ mol^{-1} above **3**, has been identified as a reasonable target for experimental observation. The equilibrium geometries of **3**–**6** are all appropriately described as 1,3,5,7,9-cyclodecapentaene and thus show no structural signs of aromaticity. The energy of the planar D_{10h} structure (**1**) of [10]annulene is found, at the 4-31G level, to decrease slightly in moving to a bond-alternating D_{5h} structure (**2**). The energy lowering, however, is not large enough for this result to be regarded as definitive. Higher levels of theory will be required to resolve the question of whether or not planar [10]annulene exhibits bond alternation. Both **1** and **2** lie considerably higher in energy than the nonplanar structures **3**–**6**.

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Molecular Mechanics Calculations and Experimental Studies of Conformations of δ-Valerolactone

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Abstract: The microwave spectrum of the title compound has been determined in the gas phase at room temperature, and the Raman spectrum has been determined on the liquid at room temperature and on the solid at 73 K. From the experimental data it is concluded that there are two conformers separated in energy by approximately 0.6 kcal/mol, and only the more stable one persists in the crystal. The more stable conformer has a very small (<0.1 D) μ_c component of the dipole moment, while this component is much greater for the less stable conformer. The rotational constants for the two conformations have been determined and are substantially different. The use of the molecular mechanics (MM2) program indicates two stable conformers, a half-chair and a boat form. The former is calculated to be 0.54 kcal/mol more stable and to have a value of μ_c about 0.02 D. The value for μ_c predicted for the boat conformer is approximately 1 D. The rotational constants calculated for the two conformations are in agreement with the experimental ones only if the half-chair conformation is the more stable.

Introduction

There have been numerous studies, both theoretical and experimental, of the conformations of cyclic molecules. Various experimental techniques including vibrational spectroscopy, rotational spectroscopy, NMR, and electron diffraction yield information relating to the identity of the stable conformations and the presence or absence of metastable conformers. Several reviews of experimental studies have appeared recently. Applications of microwave spectroscopy to small-ring molecules have been given by Gaylord and Gwinn,[2] of laser Raman studies by Wurrey et al.[3] and of Raman and far-infrared spectroscopy by Carreira et al.[4] and Malloy et al.[5] Strauss[6] has recently reviewed spectroscopic

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[1] To whom correspondence should be addressed at the University of Georgia.

[2] W. D. Gwinn and A. S. Gaylord, *MTP Int. Rev. Sci.: Phys. Chem., Ser. Two*, **3**, (1976).

[3] C. J. Wurrey, L. A. Carreira, and J. R. Durig *Vib. Spectra Struct.*, **5**, Chapter 4 (1976).

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work on medium rings. The extensive applications of NMR to the conformational analysis of medium and large rings by Anet[7] also can be noted and his reviews[8] on the eight-membered ring.

The application of our MM1 (1973) force field[9] to a study of carboxylic acids, esters, and lactones has been discussed earlier.[10] One of the compounds studied at that time was valerolactone. The calculations indicated that the boat and chair forms were both stable conformations and within about 1 kcal of each other in energy.

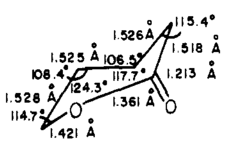
More recently, an improved force field (MM2 (1977)) has been developed for hydrocarbons[11] and subsequently extended[12] to many different functional groups, including carboxylic acids, esters, and lactones. The general approach to the parameterization was similar to that described earlier and will be published in due course. The major difference in the hydrocarbon parts of the two force fields is that the newer one has larger carbons, smaller hydrogens, and torsional potentials which contain one-, two-, and threefold potential terms. The important modification for acids and derivatives was the scaling down of the bending force constants from the spectroscopic values, as has been found consistently desirable.[9,11] The newer force field gives about the same results as the older one for the geometries of strainless molecules, but for molecules which are very distorted, the newer force field gives better results.

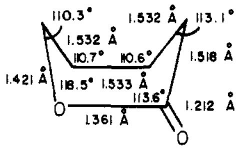
The valerolactone problem is an interesting one. At the time this work was begun, there was no experimental evidence concerning the boat/chair conformation of valerolactone itself. X-ray crystallographic structures were known for several more complicated structures which contained a valerolactone[13] ring. Interestingly, similar numbers of boat conformations and chair conformations were known from this work, in contrast to cyclohexane systems, where boats are extremely rare. This implied that the boat and chair forms of the lactone ring probably did not differ much in energy.

The above factors prompted us to undertake this joint theoretical and experimental study of the conformations of valerolactone. This was accomplished by application of the MM2 force field to the problem and by studies of the microwave spectrum and the temperature dependence of the Raman spectrum.

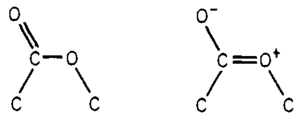
Molecular Mechanics Calculations

The application of the MM2 force field to the problem indicates that indeed the energies of the two forms are quite similar, with the chair form being a little more stable. The structures are shown





and show a number of features of interest. First, clearly there are two conflicting geometric requirements in this ring system. The ester group, that is the carbonyl carbon and both oxygens, plus the two carbons which are attached to opposite ends of the ester group all want to remain coplanar. Coplanarity permits a maximum amount of resonance of the type



and because of the double-bond character between the carbonyl carbon and the alkyl oxygen in the resonance form on the right, nonplanarity disrupts such conjugation and raises the energy of the system. On the other hand, a six-membered ring as in cyclohexane tends to adopt a chair conformation, in order to permit the ethane units to have staggered conformations. In the chair form of the lactone, these two requirements cannot be met simultaneously. There is some compromise, in that the dihedral angle about the carbonyl carbon–alkyl oxygen bond, which would prefer to be 0°, has a calculated value of 5.7°. On the other hand, the bond lengths and angles in the molecule are substantially deformed in an effort to minimize the total energy. Thus the internal ring angles at the carbonyl carbon, and at the alkyl oxygen, are opened very much beyond their normal values, while the angles at carbons 3 and 4 are compressed. These distortions lead to a substantial strain energy in this conformation (the calculated inherent strain is 4.92 kcal/mol).

On the other hand, the molecule can adopt a boat conformation (and note this is a classical boat and not a twist form as is found with cyclohexane), and while this appears in models to permit a dihedral angle of 0° about the carbonyl carbon–alkyl oxygen bond, it also requires near eclipsing at the 3–4 bond, and the hydrogens at the prow and stern on the inside of the boat are much too close together (2.48 Å). Actually, the bond angles at the carbonyl group and at the alkyl oxygen open up somewhat more than is found in a simple ester. (113.6° vs. 110.3° and 118.5° vs. 116.1°, respectively), although this is clearly in response to the fact that the bond lengths are somewhat different on this side of the ring from the bonds on the alkyl chain part of the ring. The bond angles on the alkyl side of the ring are correspondingly reduced; they have values of 110.6 and 110.7°, respectively, compared with cyclohexane (111.1°). Perhaps surprisingly, the torsional angle about the carbonyl carbon–alkyl oxygen bond is 15.9°. This is even more deformed than in the chair conformation. Not surprisingly, the energy of the chair form is less than that of the boat, by an amount calculated to be 0.54 kcal/mol.

The geometries of these ring systems are rather similar to those found for the two corresponding conformations of cyclohexene. In the latter molecule, however, the boat form is not a stable conformation (energy minimum) but rather is found on a saddle point between two mirror image chair forms. In cyclohexene, these conformations have symmetries which are C_2 and C_s, respectively. Note that the C axis of inertia in both conformations of the lactone is approximately perpendicular to the mean plane of the ring (approximately vertical as the figures are shown). An examination of the figures shows that the C component of the dipole moment would be near zero in the chair conformation, because the C=O bond is nearly perpendicular to that axis. In the boat conformation there is a sizable component along that axis, because the carbonyl group points downward. For comparison with the experimental data, the moments of inertia and corresponding rotational constants, as well as the dipole moment components in the principal axis system, were calculated for each conformer.

Experimental Section

The sample of δ-valerolactone was obtained from the Aldrich Chemical Co., Milwaukee, WI. It was used without further purification except for prolonged pumping on the sample to remove volatile impurities prior to filling the cell. Microwave spectra were obtained with Hewlett-Packard Model 8400 C and 8460 A Stark modulated microwave spectrometers with phase-sensitive detection. Due to the low vapor pressure (ca. 68 °C (5 torr)), it was not possible to increase the intensity of the lower J transitions in the ground vibrational state by lowering the temperature with dry ice. Spectra were obtained in the X-band (7.0–12.4 GHz), K-band (18–26.4 GHz), and R-band (26.4–40.0 GHz) regions. Stark effect measurements were made exclusively in the X-band region. Since the Stark effect for δ-valerolactone was quite fast, we required a

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(4) L. A. Carreira, R. C. Lord, and Thomas B. Malloy, Jr. *Top. Curr. Chem.*, 00 (1978).

(5) Thomas B. Malloy, Jr., L. E. Bauman, and L. A. Carreira, *Top. Stereochem.*, **11**, (1979).

(6) T. C. Rounds and H. L. Strauss, *Vib. Spectra Struct.*, **7** (1978).

(7) F. A. L. Anet and T. Rawdah, *Tetrahedron Lett.*, **22**, 1943 (1979), and earlier papers in this series.

(8) F. A. L. Anet, *Top. Curr. Chem.*, **45**, 170 (1974); F. A. L. Anet and R. Anet, *Dyn. Nucl. Magn. Reson. Spectrosc.*, 543 (1975).

(9) N. L. Allinger, *Adv. Phys. Org. Chem.*, **13**, 1 (1977). The MM1 program is available from Richard W. Counts, Supervisor, Quantum Chemistry Program Exchange, Chemistry Building 204, Indiana University, Bloomington, Indiana 47401. The program is No. 318.

(10) N. L. Allinger and H. Chang, *Tetrahedron*, **33**, 1561 (1977).

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

(12) This program (MM2) is also available from QCPE (ref 9), program number 395 (N. L. Allinger and Y. Yuh, *QCPE*, **12**, 395 (1980)).

(13) K. K. Cheung, K. H. Overton, and G. A. Sim, *Chem. Commun.*, 634 (1965); A. McL. Mathieson, *Tetrahedron Lett.*, 81 (1963); H. Wolfe, *ibid.*, 5151 (1966); R. N. Johnson and N. Z. Riggs, *ibid.*, 5119 (1967).

Table I. Rotational Lines Used in the Determination of Rotational Constants (MHz) for the Half-Chair Form of the δ-Valerolactone[a]

transition	obsd, MHz	obsd – calcd, MHz
	a-type	
$2_{0,2} \leftarrow 1_{0,1}$	8 476.88	0.34
$2_{1,1} \leftarrow 1_{1,0}$	9 446.98	0.10
$3_{0,3} \leftarrow 2_{0,2}$	12 314.63	0.22
$3_{1,3} \leftarrow 2_{1,2}$	11 704.87	0.42
$5_{1,4} \leftarrow 5_{1,5}$	11 116.67	0.23
$6_{2,4} \leftarrow 5_{2,3}$	28 217.28	0.15
$6_{3,3} \leftarrow 5_{3,2}$	27 566.88	0.19
$6_{4,3} \leftarrow 5_{4,2}$	26 566.02	0.06
$6_{4,2} \leftarrow 5_{4,1}$	26 680.09	0.14
$7_{0,7} \leftarrow 6_{0,6}$	26 377.75	0.04
$7_{1,6} \leftarrow 6_{1,5}$	29 759.97	0.04
$7_{1,7} \leftarrow 6_{1,6}$	26 286.66	0.15
$7_{2,6} \leftarrow 6_{2,5}$	29 000.57	0.20
$7_{2,5} \leftarrow 6_{2,4}$	32 619.77	−0.08
$7_{2,5} \leftarrow 7_{2,6}$	11 208.13	−0.05
$7_{3,5} \leftarrow 6_{3,4}$	30 678.04	−0.05
$7_{3,4} \leftarrow 6_{3,3}$	32 696.77	0.07
$7_{4,3} \leftarrow 6_{4,2}$	31 441.44	0.16
$7_{4,4} \leftarrow 6_{4,3}$	31 090.76	−0.07
$7_{5,3} \leftarrow 6_{5,2}$	30 966.95	0.07
$7_{5,2} \leftarrow 6_{5,1}$	30 986.42	0.07
$8_{0,8} \leftarrow 7_{0,7}$	29 862.90	0.21
$8_{1,8} \leftarrow 7_{1,7}$	29 841.87	0.15
	a-type	
$8_{1,7} \leftarrow 7_{1,6}$	33 151.61	0.06
$8_{2,7} \leftarrow 7_{2,6}$	32 711.58	0.13
$8_{3,6} \leftarrow 7_{3,5}$	34 809.83	−0.02
$8_{3,5} \leftarrow 7_{3,4}$	37 723.66	0.03
$8_{4,5} \leftarrow 7_{4,4}$	35 588.97	0.03
$8_{4,4} \leftarrow 7_{4,3}$	36 429.18	−0.06
$8_{5,4} \leftarrow 7_{5,3}$	35 528.82	−0.07
$8_{5,3} \leftarrow 7_{5,2}$	35 604.34	−0.19
$8_{7,1} \leftarrow 7_{7,0}$	35 221.08	−0.29
$8_{7,2} \leftarrow 7_{7,1}$	35 221.08	−0.23
$9_{0,9} \leftarrow 8_{0,8}$	33 397.35	0.09
$9_{1,8} \leftarrow 8_{1,7}$	36 570.74	−0.06
$9_{1,9} \leftarrow 8_{1,8}$	33 389.09	0.07
$9_{2,8} \leftarrow 8_{2,7}$	36 346.81	−0.02
$9_{3,6} \leftarrow 9_{3,7}$	10 457.16	0.12
$9_{3,7} \leftarrow 8_{3,6}$	38 795.76	−0.17
$9_{6,4} \leftarrow 8_{6,3}$	39 899.65	0.09
$9_{6,3} \leftarrow 8_{6,2}$	39 912.74	−0.25
$10_{0,10} \leftarrow 9_{0,9}$	36 936.28	0.14
$10_{1,10} \leftarrow 9_{1,9}$	36 932.78	−0.21
	b-type	
$2_{1,2} \leftarrow 1_{0,1}$	9 974.68	0.00
$8_{0,8} \leftarrow 7_{1,7}$	29 828.52	−0.03
$8_{1,8} \leftarrow 7_{0,7}$	29 875.63	−0.29
$9_{0,9} \leftarrow 8_{1,8}$	33 384.14	0.11
$9_{1,8} \leftarrow 8_{2,7}$	36 163.91	−0.07
$9_{1,9} \leftarrow 8_{0,8}$	33 402.24	0.00
$9_{2,8} \leftarrow 8_{1,7}$	36 753.60	−0.04
$10_{0,10} \leftarrow 9_{1,9}$	36 931.04	−0.11
$10_{1,10} \leftarrow 9_{0,9}$	36 938.24	0.26
$10_{1,9} \leftarrow 9_{2,8}$	39 856.20	−0.23

[a] $A = 4661.21$; $B = 2558.57$; $C = 1771.16$; $\kappa = -0.455\,086$.

method of calibrating the Stark cell in the X-band for low electric fields. This was accomplished by (1) calibrating the cell at high fields (>800 V/cm) using the $1 \leftarrow 0$ transition of carbonyl sulfide ($\mu = 0.7152$ D), (2) determining the dipole moment of trifluoromethylacetylene at high fields from the Stark shift of the $KM = 0$ of the $2 \leftarrow 1$ transition, and finally (3) calibrating the Stark cell at low fields using the $KM = \pm 1$ lobes of the $2 \leftarrow 1$ transition for trifluoromethyl acetylene.

The Raman spectra were obtained with a Spex Model 14018 double monochromator with laser excitation from 250 to 500 mW of the 488.0-nm line of a Spectra Physics Model 171 Argon ion laser. Raman spectra of liquid δ-valerolactone were obtained with the sample contained in a melting point capillary. Spectra of solid δ-valerolactone were obtained by spraying the sample under vacuum on a substrate in contact with a vacuum jacketed liquid nitrogen dewar fitted with Spectrosil™ windows. The sample was annealed until no changes in the spectra were noted.

(1) Results. A fast scan (ca. 10 MHz/s) of the R-band region for δ-valerolactone at a pressure of approximately 35 mtorr and a Stark field of approximately 200 V/cm is shown in Figure 1. The prominent features are a-type R-branch transitions of a prolate top for the half-chair conformation, and the values of the rotational quantum numbers, *J*, are marked on the figure. A weaker group of $8 \leftarrow 7$ transitions for the boat conformer may be seen at approximately 36.5 GHz. The corresponding group of $7 \leftarrow 6$ transitions for the boat conformer are sufficiently weaker so that they are not apparent on the high-frequency side of the corresponding transitions for the half-chair form.

(2) Half-Chair Conformation. The separation between the groups of R-branch lines for the half-chair form allows an approximate determination of B + C. Under high resolution, it was possible to find the beginning of the $7 \leftarrow 6$ series of R-branch transitions and preliminary assignments of several transitions were made. On the basis of the initial fit to the data, the assignment was confirmed by finding lines close to their predicted positions. A number of somewhat weaker b-type transitions were then assigned and included in a least-squares adjustment of the parameters. Eventually, 53 R-branch lines measured in R-band (26.4–40.0 GHz) and X-band (7.2–12.4 GHz) were included in the least-squares adjustment of the three rigid rotor constants. The *J* values of these transitions varied from $J = 1$ to $J = 10$. The assignment of the lines used in the fitting procedure along with their observed values and deviations of the calculated values are given in Table I. In the process of attempting a dipole moment determination, numerous lines in K-band (18.0–26.4 GHz) were examined. These lines were very near the predicted positions but were not measured accurately and included in the fit since it was deemed unnecessary. Extensive searches for c-type transitions yielded no lines which could be confidently assigned.

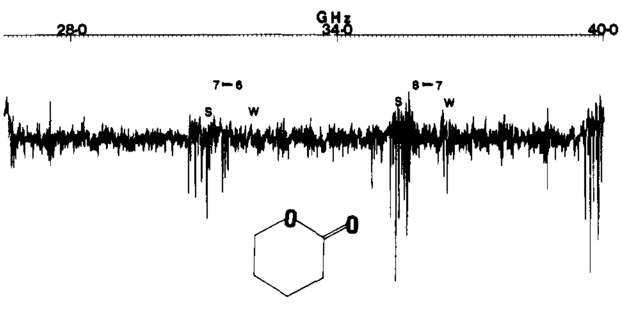

Figure 1. Survey scan of the R-band region of the microwave spectrum of δ-valerolactone (pressure = 35 mtorr; Stark field = 200 V/cm). The prominent transitions are *a*-type R-branch transitions appropriate to a prolate top. The strong (s) and weak (w) series are due to the half-chair and boat conformation, respectively.

With some difficulty we located three low *J* transitions in the X-band region which were suitable for Stark effect measurements. We were aided by preliminary predictions of the Stark effect based on bond moment calculations of the dipole moment components for the half-chair form. Although these were considerably in error, the trends predicted allowed us to locate and follow the Stark lobes in a rather dense spectrum.

A total of six Stark lobes for three low *J* transitions in the X-band region were used to determine the dipole moment components $|\mu_a|$ and $|\mu_b|$ for the half-chair form of δ-valerolactone. The transitions and $|M|$ values of the lobes are listed in Table II. The Stark effect for these lobes were second order over the range of electric fields used, from approximately 150 to 1100 V/cm. Stark displacements up to 90 MHz for some lobes were measured. The Stark coefficients determined individually for the various lobes along with their dispersions (twice the standard deviations) are given in Table II.

The second-order Stark effect for a given transition is given by eq 1, where the $\Delta\alpha$'s and $\Delta\beta$'s are functions of the rotational constants and the

$$\Delta\nu_M = (\Delta\alpha_a + \Delta\beta_a M^2)\mu_a^2 E^2 + (\Delta\alpha_b + \Delta\beta_b M^2)\mu_b^2 E^2 + (\Delta\alpha_c + \Delta\beta_c M^2)\mu_c^2 E^2 \quad (1)$$

particular levels involved in the the transitions. M is the quantum number of the Z projection of the total angular momentum in a space-fixed axis system. The μ's are the components of the dipole moment vector, and E is the electric field.

The $\Delta\alpha$'s and $\Delta\beta$'s were calculated for the transitions in Table II in the standard fashion. It was found for the transitions involved that the dependance of the Stark displacements on μ_c was minimal. Consequently, we were able to fit the 39 measured Stark displacements for the six lobes by least-squares adjustment of $|\mu_a|$ and $|\mu_b|$, assuming no contribution to the Stark displacement from the third term in eq 1 which involves $|\mu_c|$. The calculated Stark coefficients ($10^6\Delta\nu/E^2$) shown in Table II lie within the dispersions of those measured individually.

Extensive searches for transitions which would allow determination of μ_c resulted in failure. We particularly concentrated on examining several transitions of the form $(J+1)_{0,J+1} \leftarrow J_{0,J}$ and $(J+1)_{1,J+1} \leftarrow J_{1,J}$. For $|M| = 0$, the coefficients of μ_c^2 are predicted to be 2–3 orders of magnitude greater than the coefficients of μ_a^2 and μ_b^2. These pairs of transitions are predicted to have mirror-image Stark effects having a strong dependence on μ_c. We searched extensively, particularly in the K-band region, but were unable to follow the Stark lobes more than a few megahertz and consequently could not make a reliable assignment of the $|M|$ values. However, since rather high fields were required to modulate these lines, we were able to conclude that $|\mu_c|$ is quite small for the half-chair conformation and that a good estimate of the total dipole moment may be obtained from μ_a and μ_b above. This is given in Table II as 4.71 D.

(3) **Boat Conformation.** The assignment of the lines for the determination of the rotational constants for the boat conformation proceeded along the same path outlined above for the half-chair conformer. Table III gives the assignment, observed values, and deviations for the 48 transitions measured in the X- and R-bands which were used in the least-squares determination of the three rotational constants.

Due to the fact that the lines for this conformer are weaker than those of the half-chair form, we were unable to follow the Stark effect of low J transitions in X-band and, consequently, were unable to determine the dipole moment. However, we were able to conclude from a qualitative study of the Stark effect for $(J+1)_{0,J+1} \leftarrow J_{0,J}$ and $(J+1)_{1,J} \leftarrow J_{1,J}$ pairs that μ_c for this conformer is considerably greater than for the half chair conformer.

Figure 2 shows the $6_{06} \leftarrow 5_{05}$ transition for the half-chair conformer at various values of the electric field. This figure illustrates what we had said about the difficulty of finding suitable transitions for measuring the Stark effect. However it appears that as the field is increased, Stark lobes appear on the low-frequency side of the line. It is also apparent that relatively high fields are required to modulate this line. Figure 3 shows the same transition for the boat conformer at the same values of the field. Again it appears that Stark lobes move out to low frequencies from this line. It is also apparent that the transition for this conformer is modulated at much lower fields than for the half-chair conformer.

We calculated the coefficients appearing in eq 1 for the Stark effect for the $6_{06} \leftarrow 5_{05}$ transition for each conformer. These are given in Table IV. The large value of $\Delta\beta_c$ is due to the proximity of the pairs of levels, 6_{06}, 6_{16} and 5_{05}, 5_{15}. At high fields, deviation from a second-order effect is expected and should be dealt with by using the degenerate perturbation theory. However, for our purposes, consideration of a second-order effect is sufficient.

For purposes of illustration, we have considered the predicted dependence of the $|M| = 3$ lobes for the two conformers. The Stark coefficients for these lobes are given by eq 2 for the half-chair conformer and eq 3

$$10^6\Delta\nu_3/E^2 = +0.166\mu_a^2 + 0.759\mu_b^2 - 226\mu_c^2 \quad (2)$$

$$10^6\Delta\nu_3/E^2 = +0.170\mu_a^2 + 0.780\mu_b^2 - 241\mu_c^2 \quad (3)$$

for the boat conformer. It is clear that even a small value of μ_c can have a major effect. Since we know μ_a and μ_b for the half-chair conformer, we can make some statement on the magnitude of μ_c. If $|\mu_c| = 0.05$D, the negative contribution of the μ_c^2 term very nearly cancels the positive contributions of the μ_a^2 and μ_b^2 terms. On the otherhand, if $|\mu_c|$ is greater, it will dominate the Stark effect and lead to modulation of the lines at quite low fields. Our conclusion is that $|\mu_c|$ is of the order of a tenth of a debye for the half-chair form. Consequently, the approximation

$$\mu^2_{\text{total}} \approx \mu_a^2 + \mu_b^2 \quad (4)$$

is certainly justified.

On the other hand, we were not able to determine $|\mu_a|$ and $|\mu_b|$ from Stark effect data for the boat conformation. However, they should be similar for those of the chair form. Regardless of the ring conformation, the a-axis, corresponding to the smallest moment of inertia, will be very nearly colinear with the carbonyl group. Certainly μ_a will be dominated by the presence of the carbonyl group. Figure 3 shows the $6_{06} \leftarrow 5_{05}$ transition for the boat conformation at the same values of the field used for the half-chair conformation in Figure 2. We are almost certainly observing Stark lobes on the low-frequency side of this line which can only be explained as arising from a dominance of the μ_c^2 term in eq 3. When Figures 2 and 3 are compared it is seen that the boat conformer has a much faster Stark effect for this transition. We believe that this is good, if indirect, evidence for a sizable μ_c component of the dipole moment. This point will be further discussed below.

Table II. Stark Coefficients, $10^6\Delta\nu/E^2$ (in MHz cm^2/V^2), and Dipole Moment Components of the Half-Chair Form of δ-Valerolactone[a]

transition	$\|M\|$	$10^6\Delta\nu/E^2$ obsd	$10^6\Delta\nu/E^2$ calcd
$2_{0,2} \leftarrow 1_{0,1}$	0	−173.0 ± 7	−175.0
	1	+180.0 ± 3	+182.0
$3_{1,3} \leftarrow 2_{1,2}$	1	+66.1 ± 6.5	+61.7
	2	+27.6 ± 3.2	27.3
$3_{0,3} \leftarrow 2_{0,2}$	0	−28.0 ± 1.9	−26.9
	2	+84.4 ± 3.4	+84.5

[a] $|\mu_a| = 4.53 \pm 0.02$ D; $|\mu_b| = 1.30 \pm 0.03$ D; $|\mu_c| = 0.0$ (assumed); $\mu_{\text{total}} = 4.71$ D.

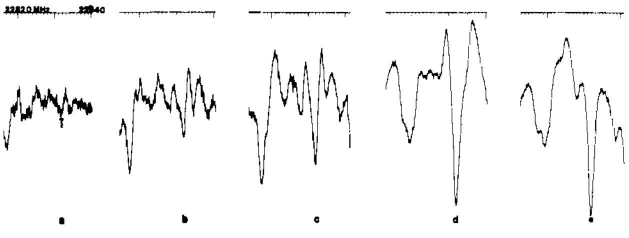

Figure 2. Stark effect of the $6_{06} \leftarrow 5_{05}$ transition for the half-chair form. The arrows mark the position of the line and the region where the Stark lobes appear, respectively: (a) 100 V/cm; (b) 200 V/cm; (c) 300 V/cm; (d) 1000 V/cm; (e) 1600 V/cm.

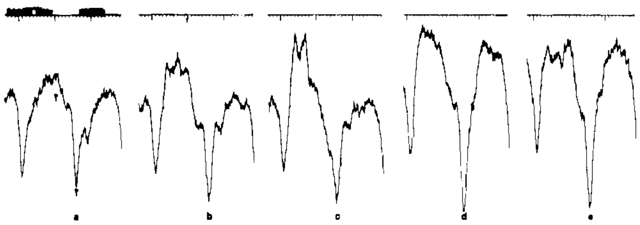

Figure 3. Stark effect of the $6_{06} \leftarrow 5_{05}$ transition for the boat form. The arrows mark the position of the line and the region where the Stark lobes appear, respectively: (a) 100 V/cm; (b) 200 V/cm; (c) 300 V/cm; (d) 1000 V/cm; (e) 1600 V/cm. The different parts of this figure should be compared to the corresponding parts of Figure 2. The amplifier gain for the spectra in this figure was approximately 3 times that in Figure 2.

(4) **Raman Spectra.** We had hoped to be able to estimate the ΔH between the half-chair and boat conformers by comparing intensities of rotational lines in the microwave spectrum. However, this required a knowledge of the dipole moment components of both conformers. Since we were not able to determine the dipole components of the boat form, we were unable to follow this procedure.

To confirm that we were dealing with a case of an equilibrium mixture of conformers and to rule out the possibility of one of the sets of rotational lines being due to an impurity, we performed a series of Raman experiments. Figure 4 is Raman spectrum of liquid δ-valerolactone at room temperature. Particularly prominent is a pair of lines at 748 and 798 cm^{-1}, which we have assigned as the ring-breathing vibrations of the half-chair and boat conformations, respectively. This assignment was based on the fact that the line at 798 cm^{-1} was not present in the spectrum of a solid sample at 73 K. Figure 5 is the Raman spectrum of solid δ-valerolactone at liquid-nitrogen temperature. A number of lines appear as symmetric doublets characteristic of crystal splitting. We have marked the position of the ring-breathing mode for the half-chair conformation. The frequency in the solid phase is approximately 5 cm^{-1} higher than in

Table III. Rotational Lines Used in the Determination of the Rotational Constants (MHz) for the Boat Form of the δ-Valerolactone

transition	obsd, MHz	obsd – calcd, MHz
	a-type	
$2_{0,2} \leftarrow 1_{0,1}$	8 758.90	0.06
$2_{1,1} \leftarrow 1_{1,0}$	9 655.93	0.45
$3_{1,3} \leftarrow 2_{1,2}$	12 203.10	−0.53
$5_{1,4} \leftarrow 5_{1,5}$	10 281.13	−0.27
$6_{1,5} \leftarrow 5_{1,4}$	27 068.52	0.07
$6_{2,4} \leftarrow 5_{2,3}$	28 852.86	0.05
$6_{3,3} \leftarrow 5_{3,2}$	28 246.18	0.04
$6_{4,2} \leftarrow 5_{4,1}$	27 428.59	−0.06
$6_{4,3} \leftarrow 5_{4,2}$	27 324.39	0.20
$7_{0,7} \leftarrow 6_{0,6}$	27 577.62	0.21
$7_{1,7} \leftarrow 6_{1,6}$	27 529.64	0.11
$7_{1,6} \leftarrow 6_{1,5}$	30 746.91	−0.04
$7_{2,5} \leftarrow 7_{2,6}$	10 354.85	0.10
$7_{2,6} \leftarrow 6_{2,5}$	30 040.25	0.16
$7_{3,4} \leftarrow 6_{3,3}$	33 449.38	−0.23
$7_{3,5} \leftarrow 6_{3,4}$	31 589.18	0.11
$7_{4,4} \leftarrow 6_{4,3}$	31 968.21	−0.03
$7_{4,3} \leftarrow 6_{4,2}$	32 289.40	−0.17
$7_{5,2} \leftarrow 6_{5,1}$	31 871.45	−0.03
$7_{5,3} \leftarrow 6_{5,2}$	31 853.62	0.28
$8_{0,8} \leftarrow 7_{0,7}$	31 297.00	0.06
$8_{1,7} \leftarrow 7_{1,6}$	34 343.45	0.03
$8_{1,8} \leftarrow 7_{1,7}$	31 277.40	0.11
$8_{2,6} \leftarrow 7_{2,5}$	37 571.59	−0.11
$8_{2,7} \leftarrow 7_{2,6}$	33 932.80	0.03
$8_{3,6} \leftarrow 7_{3,5}$	35 871.00	−0.15
	a-type	
$8_{3,5} \leftarrow 7_{3,4}$	38 559.60	−0.38
$8_{4,4} \leftarrow 7_{4,3}$	37 358.88	−0.40
$8_{4,5} \leftarrow 7_{4,4}$	36 587.78	−0.24
$8_{5,3} \leftarrow 7_{5,2}$	36 600.34	−0.09
$8_{5,4} \leftarrow 7_{5,3}$	36 531.49	0.17
$8_{7,1} \leftarrow 7_{7,0}$	36 247.81	0.15
$8_{7,2} \leftarrow 7_{7,1}$	36 247.72	0.11
$9_{0,9} \leftarrow 8_{0,8}$	35 025.46	0.05
$9_{1,9} \leftarrow 8_{1,8}$	35 017.67	−0.00
$9_{1,8} \leftarrow 8_{1,7}$	37 964.74	−0.00
$9_{2,8} \leftarrow 8_{2,7}$	37 755.31	0.07
$10_{0,10} \leftarrow 9_{0,9}$	38 757.59	−0.32
$10_{1,10} \leftarrow 9_{1,9}$	38 754.79	−0.16
	b-type	
$2_{2,1} \leftarrow 2_{1,2}$	8 038.02	0.41
$4_{1,3} \leftarrow 4_{0,4}$	7 528.50	0.17
$4_{3,1} \leftarrow 3_{2,2}$	29 972.40	0.24
$7_{3,5} \leftarrow 6_{2,4}$	38 532.90	−0.20
$8_{0,8} \leftarrow 7_{1,7}$	31 265.10	0.24
$8_{1,7} \leftarrow 7_{2,6}$	33 551.65	0.06
$8_{2,6} \leftarrow 7_{3,5}$	32 426.07	0.43
$9_{4,5} \leftarrow 9_{3,6}$	11 404.31	0.05
$10_{4,6} \leftarrow 10_{3,7}$	11 453.22	−0.11

[a] $A = 4547.06$; $B = 2595.87$; $C = 1867.86$; $\kappa = -0.456545$.

Table IV. Coefficients[a] for the Stark Effect of the $6_{06} \leftarrow 5_{05}$ Transitions for the Two Conformers of δ-Valerolactone

conformer	$10^6 \Delta\alpha_a$	$10^6 \Delta\beta_a$	$10^6 \Delta\alpha_b$	$10^6 \Delta\beta_b$	$10^6 \Delta\alpha_c$	$10^6 \Delta\beta_c$
half-chair	−0.1405	+0.0344	−0.0775	+0.0926	+0.0648	−25.13
boat	−0.1350	+0.0339	−0.1068	+0.0985	+0.0607	−26.76

[a] See eq 1 for definition of parameters.

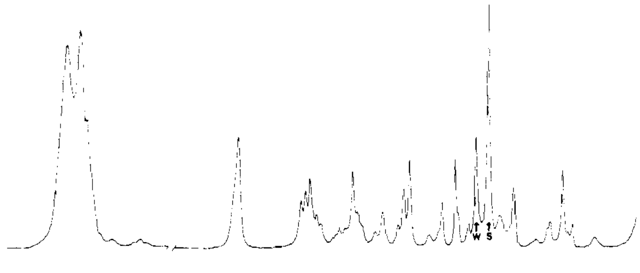

Figure 4. Raman spectrum of liquid δ-valerolactone (excitation = 500 mW at 488 nm; resolution = ca. 2 cm^{-1}). The ring-breathing modes for the half-chair (s) and boat (w) conformers are marked in the figure.

the liquid phase. We have also marked the expected position of the ring-breathing mode for the boat conformation. There is no Raman line observed within 40 cm^{-1} on either side of this position. This is conclusive evidence that we are dealing with two conformers.

We attempted to determine ΔH by measuring the relative intensities of the two ring-breathing modes in the liquid sample for a series of temperatures from room temperature up to 100 °C.[14] A very small increase of the intensity of the line assigned to the boat form was observed. However, the precision of the data did not allow an accurate determination of ΔH. We then compared the intensities of the two lines at room temperature, made the assumption that the derivatives of the polarizability with respect to the ring-breathing coordinates were the same, and calculated a ΔH of approximately 200 cm^{-1} (~0.6 kcal/mol). The ratio of two lines arising from conformers separated by this amount is predicted to be 0.37 at 25 °C and 0.44 at 100 °C. This was comparable to our observations, but we could not accurately measure this small change. However, we feel confident that 200 cm^{-1} is a reasonable estimate of the value of ΔH. The fact that the prominent a-type lines in the microwave spectrum (Figure 1) are approximately 3 times as intense as the corresponding lines for the boat form is consistent with a ΔH of approximately 200 cm^{-1} if the values of μ_a are approximately equal for the two conformers.

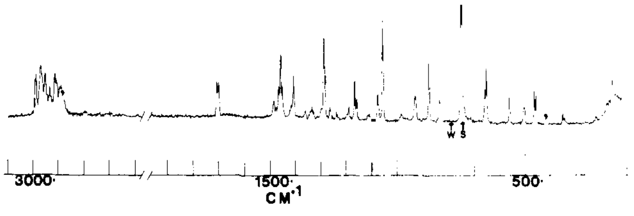

Figure 5. Raman spectrum of solid δ-valerolactone (excitation = 500 mW at 488 nm; resolution = ca. 2 cm^{-1}; temperature = 73 K). The ring-breathing mode for the half-chair form is indicated by the arrow. The expected position of this mode for the boat form is shown.

Table V

rotational constants, MHz	half-chair calcd	half-chair exptl	boat calcd	boat exptl
A	4653	4661.21	4408	4547.06
B	2539	2558.57	2625	2595.87
C	1767	1771.16	1883	1867.86

dipole moment, D	half-chair calcd	half-chair exptl	boat calcd
μ_a	4.02	4.53	3.90
μ_b	0.71	1.30	0.62
μ_c	0.01	~0.1	0.96[a]
μ_{total}	4.08	~4.71	4.06

[a] Experimentally found to be significantly greater than μ_c for the half-chair form.

Discussion of the Results

Table V gives the rotational constants determined from the microwave data, as well as those calculated from the moments

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(14) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis", Wiley-Interscience, New York 1965, p 146.

of inertia of the structures determined by using the MM2 program. The agreement is quite good.

In our force field calculations of molecules other than hydrocarbons, a bond-moment scheme[12] is used in order to calculate dipole moments and point dipoles are used to represent the bond moments. an electrostatic calculation, originally due to Jeans and subsequently modified,[9,15] was employed to estimate electrostatic energies, which must be included in the calculations.

Bond-moment schemes for calculating dipole moments have long been used, and they are in general semiquantitative in their results.[9] One reason for their limited accuracy is that they only allow for the standard moments between atom pairs. The induced moments which result when a sizable dipole is placed into a highly polarizable environment are not taken into account. Our force field dipole–dipole calculations[9,11] are of this sort. In practice such calculations prove to be adequate for predicting structures. For energies and for dipole moments, the results are often only semiquantitative. Nonetheless, this is the scheme used by our molecular mechanics program.

Because of the discrepancy between the dipole moment for the lactone calculated by this method (3.81 D) and that found experimentally (4.71 D), we decided to have a look at a more refined technique for dipole moment calculation. This is a procedure originally due to Eyring,[16] and it is subsequently modified and extended.[17] In the latest version,[18] it permits one to allow completely for the induced moments throughout the molecule. This procedure gives dipole moments in complex polar molecules which are substantially better than one gets by the simple bond-moment scheme. In the present case, the calculated total moment is indeed appreciably improved, although the agreement with experiment is still not very good. The remaining error is believed to result from the fact that ether and ketone components for the original bond moments are used. Thus they did not account for the ester resonance, and the calculated moments are too small. The results are given in Table V.

In summary, the experimental data show that there are two conformers separated in energy by approximately 0.6 kcal/mol with the more stable conformer having a very small (<0.1 D) μ_c component of the dipole moment. The less stable conformer has a much greater value of μ_c. The rotational constants have been determined from the microwave data.

The use of the MM2 program indicates two stable conformers, a half-chair and a boat form. The half-chair form is calculated to be 0.54 kcal/mol more stable than the boat and to have a value of μ_c of the order of 0.01–0.02 D. In addition, the rotational constants for this half-chair conformer are in good agreement with those determined experimentally for the more stable conformer. The values of μ_c predicted for the boat conformer (0.96–1.06 D) are in agreement with the qualitative experimental result on the magnitude of μ_c for the less abundant conformer. The calculated rotational constants for this boat conformer are in agreement with those found experimentally from the microwave spectrum.

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(15) J. M. Lehn and G. Ourrison, *Bull. Soc. Chim. Fr.*, 1113 (1963).

(16) R. P. Smith and H. Eyring, *J. Am. Chem. Soc.*, **74**, 229 (1952), and subsequent papers.

(17) N. L. Allinger and M. T. Wuesthoff, *Tetrahedron*, 33, 3 (1977); L. Dosen-Micovic and N. L. Allinger, *ibid.*, **34**, 3385 (1978).

(18) L. Dosen-Micovic, thesis submitted to the University of Belgrade, 1979.

Direct Measurements of Tetraphenylethylene Torsional Motion by Picosecond Spectroscopy

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Abstract: We have investigated the *time*- and *wavelength*-resolved fluorescence of tetraphenylethylene (TPE) induced by 355-nm picosecond excitation in several solvents over a range of temperatures and viscosities. Several distinct fluorescence kinetic processes have been identified that are manifested by (i) time-dependent fluorescence spectral shifts, (ii) time-dependent fluorescent spectral-shape changes, and (iii) nonexponential fluorescence decay kinetics. It is found that the relaxation rates of these processes depend strongly on temperature and solvent viscosity. Two of the processes have rates that are greater than 10^{12} s^{-1} at room temperature. The observed fluorescence dynamics of TPE are complex and suggest that several channels are available for excited-state relaxation. We have tentatively assigned the relaxation pathways to radiative and radiationless electronic decay, vibrational relaxation, and two forms of excited-state conformational relaxation. A unified model is proposed for the photochemical dynamics of TPE.

In a photochemical reaction the electronically excited starting material is converted to the stable photoproducts by a number of relaxation processes. The most widely studied and best understood of these are fluorescence and phosphorescence. A considerable effort has also been expended in the study of radiationless vibrational and electronic transitions, which have recently been monitored directly by means of picosecond spectroscopy.[1-3] One of the least studied processes, in contrast, is excited-state conformational relaxation, which is commonly believed to be significant for photochemical reactions in which the starting material and product stereochemistry greatly differ. Examples include cis–trans isomerization[4] and intramolecular cyclization.[5]

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(1) P. F. Barbara, L. E. Brus, and P. M. Rentzepis, *Chem. Phys. Lett.* **69**, 447 (1980).

(2) P. F. Barbara, P. M. Rentzepis, and L. E. Brus, *J. Chem. Phys.*, **72**, 6802 (1980).

(3) For examples of picosecond studies of electronic radiationless decays: (a) L. J. Noe, E. O. Degenkolb, and P. M. Rentzepis, *J. Chem. Phys.*, **68**, 4435 (1978); (b) K. G. Spears and M. El-Manguch, *Chem. Phys.*, **24**, 65 (1977); (c) H. B. Lin and M. Topp, *Chem. Phys. Lett.*, **64**, 452 (1979).

(4) (a) G. Fischer, G. Seger, K. A. Muszkat, and E. Fischer, *J. Chem. Soc., Perkin Trans. 2*, 1569 (1975); (b) M. A. El-Bayoumi and F. M. Abdel-Halim, *J. Chem. Phys.*, **48**, 2536 (1968); (c) H. Stegemeyer, *Chem. Ber.*, **72**, 335 (1968); (d) J. Kordas and A. El-Bayoumi, *J. Am. Chem. Soc.*, **96**, 3043 (1974). (e) C. O. DeBoer and R. Y. Schlessinger, *ibid.*, **90**, 803 (1968); J. Salliel, O. C. Zafirious, E. D. Megarity, and A. A. Lamola, *ibid.*, 4759 (1968).

(5) D. Billen, N. Boens, and F. C. De Schrijver, *J. Chem. Res. Synop.*, 79 (1979); F. B. Mallory, J. T. Gordon, and C. S. Wood, *J. Am. Chem. Soc.*, **85**, 828 (1963); **86**, 3094 (1964); E. Fischer and K. A. Muszkat, *J. Chem. Soc. B.*, 662 (1967); E. Fischer, *Fortschr. Chem. Forsch.*, **7**, 605 (1967).