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Structure, Molecular Orbital Calculation, and Experimental Evidence for the 1-3-Propiolactone

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With 4 Figures and 3 Tables   (Received 31st January 1973)

Abstract

The structural parameters for the 1–3 propiolactone are determined from the A, B, and C rotational constants. These parameters are used in a CNDO/2 calculation for getting dipolar moment and also electronic, total, binding and orbital energies. The obtained results are compared with the available experimental evidence.

The 1-3-propiolactone or β-propiolactone has been studied in connection with its applications in bactericide compounds [1, 2] and as a cancerigen agent [3–5]. It is a strained four-membered ring compound whose unusual chemical and physical properties have been the subject of a number of investigations [1–17]. A unique feature of the β-lactones is the occurrence of the alkyl C—O bond fission during hydrolysis in neutral or slightly acid media. This has been attributed to ring strain since all higher lactones exhibit rupture of the acyl C—O bond exclusively [8]. Structural studies indicate that in propiolactone the later bond is abnormally long, $1 \cdot 43A$ as compared to $1 \cdot 36A$ in methyl acetate [11]. Delocalization of the ring electrons has been suggested as a possible explanation of the observed uniformity of the ring distances. Comparision of the dipole moment of β-propiolactone and γ-butyrolactone in solution, $3 \cdot 8d$ [12] and $4 \cdot 12d$ [18], respectively, has led to the suggestion that the transfer of the ring oxygen lone pair electrons is smaller in the former compound.

In our laboratory it is one of the molecules we are systematically studying from several view-points, using microwave spectroscopy and molecular orbitals calculation technics.

In this communication we report some results obtained from the application of CNDO/2 calculations using a molecular structure evaluated by us from microwave spectra (Fig. 1).

Among the results obtained, the dipolar moment calculation gives a quite acceptable approximation to the experimental results given by Boone et al. [16], considering the large deviations from actual values that we are used to obtain from semiempirical methods like CNDO, specially for molecules other than diatomics.

In Table 1, the rotational constants taken from the microwave spectrum are compared with the calculated ones for the molecular structure that we propose in Fig. 1, after several trials for fitting the experimental values.

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Table 1. Experimental rotational constants. Calculated values from the structure given in Fig. 1 (MC/S)

	Experimental	Calculated
A	12,406·04	12,406·037
B	5,244·46	5,244·424
C	3,869·17	3,869·283
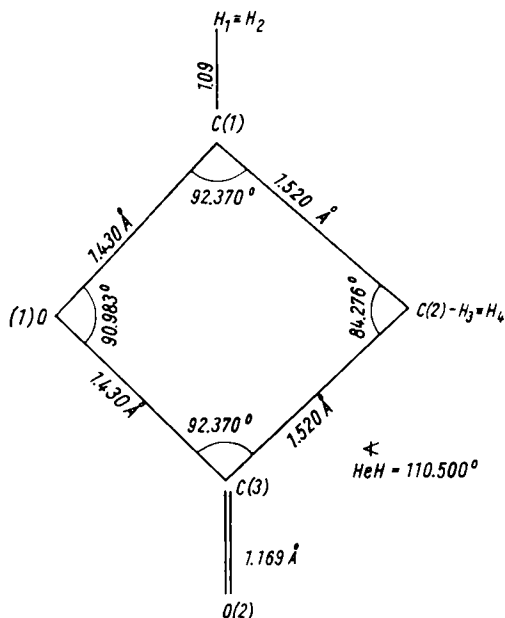
Fig. 1. Structural parameters of 1–3 propiolactone, the planes HeH are perpendicular to the plane of the paper and bisect the corresponding angles. The direction C|3|O|2| bisects the angle $O_{|1|}C_{|3|}C_{|2|}$

In Table 2, there can be seen the experimental and theoretical values for the dipolar moment, and the absolute and percentual differences relative to the experimental data; a, b, c are the principal axes for the inertia tensor (see also Fig. 2).

Table 2. Experimental and calculated values for the dipole moments, and absolute and percentual difference relative to experimental data.
(a, b and c are the principal axes for the inertia tensor)

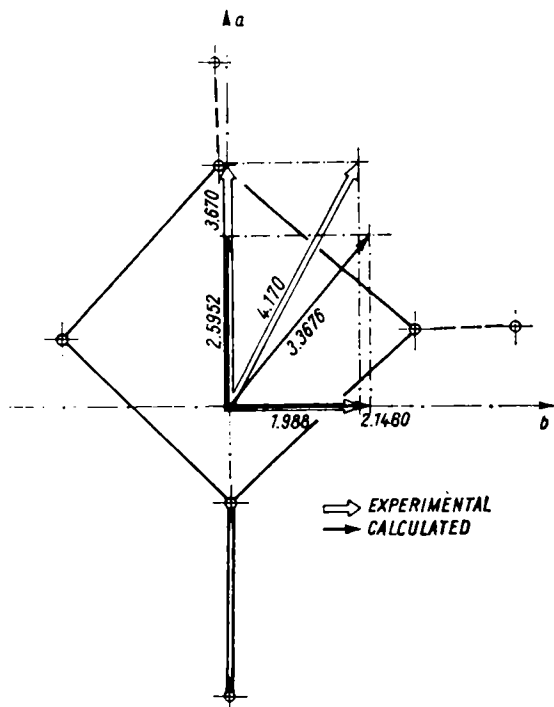|	Experimental	Calculated	$\Delta\mu = \mu_{exp.} - \mu_{calc.}$	$\delta\mu\% = \dfrac{\Delta\mu}{\mu_{exp.}} \times 100$
	Debyes	Debyes	Debyes	%
μ_c	0·000	0·0000	0·000	0
μ_b	1·988	2·1460	−0·158	−8
μ_a	3·670	2·5952	1·075	29
μ	4·174	3·3676	0·806	19

Fig. 2. Experimental and calculated values for the dipolar moment and its components in the principal axes system (in Debyes)

The results obtained for the electronic, total, binding and orbital energies are given in Table 3.

Table 3. Calculated energies (A.u.)

	Calculated	Experimental
Electronic energy	−153·4421	
Total energy	−61·1628	
Binding energy	−3·9490	≈ −1433·7 kcal/mol

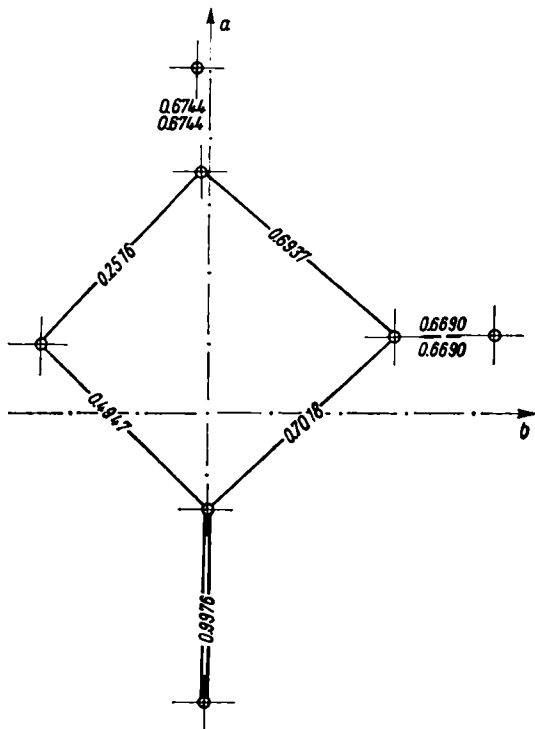|	Orbital energies		
Occupied orbitals		Unoccupied orbitals	
−1·9004	−0·9026	−0·5358*	0·2824
−1·6159	−0·8166	−0·4779	0·3180
−1·3435	−0·7040*	0·1582*	0·3621*
−1·1108	−0·6786*	0·2533	0·3691
−1·0194*	−0·6492	0·2677	0·4016*
−0·9119	−0·5702	0·2774*	0·5322

* for Pi orbitals
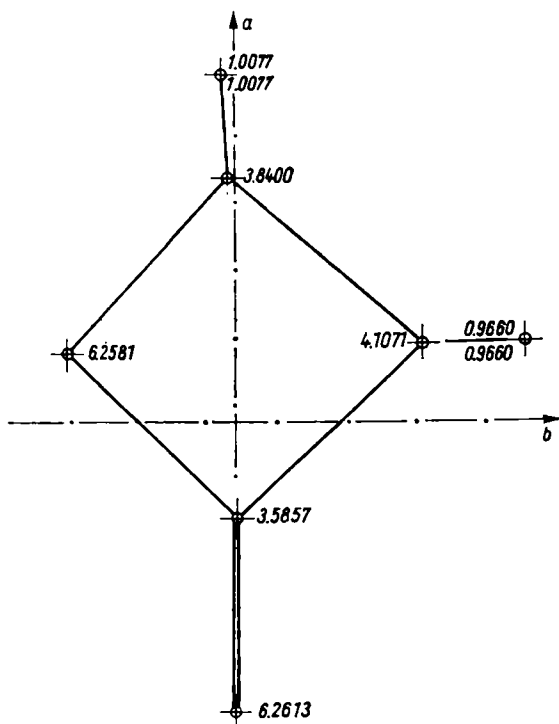
Fig. 3. Bond orders for adyacent atoms

Fig. 4. Electronic charges centered on each atom

In addition, in Figs. 3 and 4 we give the bond orders for neighbour atoms and the electronic charge centered on each atom, respectively.

In conclusion, from the comparative analysis of the experimental values with the calculated ones, we observe that the error in the dipolar moment calculation is principally due to a large subvaluation (29%) in μ_a calculation. Hence we can suppose that the actual M.O.'s are such that the electronic charge distribution is slightly shifted towards the $O_{(2)}$ zone with respect to what is suggested by the values in Fig. 4. For the same reason we could think that the actual double bond character in the $C_{(3)}$—$O_{(2)}$ bonding is slightly higher than suggested by the corresponding bond order in Fig. 3.

Lastly, considering that the structural parameters are very good approximated, the binding energy is grossly overestimated by the used method. On the other hand, Fig. 3 shows that the C—O alkyl bond is the weakest one, which is a remarkable agreement with experience.

References

[1] Hoffman, R. K.: Appl. Microbiol. **16** (4) (1968) 641.
[2] Veselov, M. P., and A. I. Osipova: Zh. Mikrobiol. Epidemiol. Immunobiol. **44** (12) (1967) 83 (russ.).
[3] Colburu, N. H., and R. K. Boutwell: Cancer Res. **28** (4) (1968) 642.
[4] Colburu, N. H., and R. K. Boutwell: Cancer Res. **28** (4) (1968) 653.
[5] Hemings, H., H. C. Smith, N. H. Colburu and R. K. Boutwell: Cancer Res. **28** (3) (1968) 543.
[6] Gresham, T. L., J. E. Jansen and F. W. Shaver: J. Am. Chem. Soc. **70** (1948) 998.
[7] Bartlett, P. D., and G. Small: J. Am. Chem. Soc. **72** (1950) 4867.
[8] Davies, A. G., and J. Kenyon: Quart. Revs. (London) **9** (1955) 203.
[9] Searles, S., M. Tamres and G. M. Barrow: J. Am. Chem. Soc. **75** (1953) 71.
[10] Friedman, L., and F. A. Long: J. Am. Chem. Soc. **75** (1953) 2832.
[11] Bregman, J., and S. H. Bauer: J. Am. Chem. Soc. **77** (1955) 1955.
[12] Miller, R. F.: Phys. Rev. **89** (A) (1953) 341.
[13] Boggia, L. M., P. G. Favero and O. M. Sorarrain: Chem. Phys. L. **12** (2) (1971) 382.
[14] Boggia, L. M., O. M. Sorarrain, R. R. Filgueira and M. C. Villani: An. Asoc. Quim. Arg. (Buenos Aires) **59** (1971) 309.
[15] Gresham, T. L., J. E. Jansen, F. W. Shaver, M. R. Frederick, F. T. Fiodorek, R. A. Bankert J. T. Gregory and W. L. Beears: J. Am. Chem. Soc. **74** (1952) 1323.
[16] Boone, D. W., C. O. Britt and J. E. Boggs: J. Chem. Phys. **43** (4) (1965) 1190.
[17] Kwak, N., J. H. Goldstein and J. W. Simons: J. Chem. Phys. **25** (6) (1956) 1203.
[18] Marsden, R. J. B., and L. E. Sutton: J. Chem. Soc. (London) **1936** 1383.