

CONFORMATIONAL ANALYSIS OF SOME ACRYLATES USING DIPOLE MOMENT CALCULATIONS BY CNDO/FORCE METHOD

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Abstract—CNDO MO calculations are carried out for four acrylates, $H_2C=C(R_1)-COO(R_2)$ with $R_1=H$, Me and $R_2=Me$, Et for dipole moment determination using the Pople-Segal expression.⁷ Energy minimization for various conformers in each molecular system was achieved by the gradient method. Dipole moments for comparatively stable conformers of each of the molecules considered are reported. Theoretically calculated energy values are used to arrive at the equilibrium geometry and the corresponding dipole moments are compared with the experimental values in each system considered.

Dipole moments of several acrylates have been reported.^{1,2} The dielectric permittivity ϵ' and loss factor ϵ'' were determined for methyl acrylate, ethyl acrylate, methyl methacrylate and ethyl methacrylate at different temperatures and microwave frequencies.¹ The activation energies and relaxation times were estimated. It was observed that the absorption maxima for these liquids are in the millimeter region. The dipole moments were calculated using Onsager's equation and Rao's equation. In the latter paper,² the relaxation times and dipole moments of these acrylates were determined using single-frequency method of Sobhanadri. It is observed, in general, that the dipole moments obtained by Guggenheim's relation² are larger than the dipole moments calculated using Onsager's and Rao's equations. In some of the studies³ Higasi relation has been used for the estimation of the dipole moment of organic systems.

As an extension to our programme of studies of dipole moments of organic systems, we report here the results of our theoretical investigation carried out on four monomeric acrylates. Many semi-empirical MO theories have been tried successfully in predicting equilibrium geometries and various ground and excited state properties of several molecular systems have since been calculated. A given set of parameters used in the MO calculations are good only for determining certain molecular properties. For example, Del Bene and Jaffe⁴ have used a set of parameters entirely different from the ones originally proposed by Pople⁵⁻⁷ for calculating spectral transitions and ionization potentials using CNDO (Complete Neglect of the Differential Overlap) method.⁵ Pople-Segal formula for dipole moments in the CNDO approximation is considered as the most accurate one of several approximate formulae satisfying the requirements of translational invariance.⁸ Such calculations are particularly successful when the molecules involved have simple atoms like C or H, as

in the case of monosubstituted benzene or aliphatic molecules like formaldehyde. These calculations have also been used to predict dipole moment derivatives and thus IR intensities of a number of simple molecular systems.^{9,10} Recent investigations of Pulay¹¹ and Kanakavel *et al.*¹² demonstrate that gradient method in CNDO calculations leads to better convergence, energy minimization and more effective evaluation of MO's. In the present studies, a modified version of CNINDO programme called CNDO/Force is used to calculate the electric dipole moment of four monomeric acrylates and these calculations are used to arrive at the correct molecular conformations.

Method of calculation

The application of CNDO method for determining the molecular dipole moment leads to the following formula⁴

$$\mu = \mu_{\text{charge}} + \mu_{\text{hyb}}$$

μ_{charge} is the contribution due to net atomic charge densities which is given by

$$\mu_{\text{charge}} = 2.5416 \sum_A \Delta P_{AA} \bar{R}_A \quad \text{Debye}$$

where \bar{R}_A is the position vector of the nucleus A and $\Delta P_{AA} = Z_A - P_{AA}$; P_{AA} is the self-consistent electron density on atom A and Z_A its core charge. ΔP_{AA} is thus the net atomic charge on the atom A .

μ_{hyb} is the contribution from atomic polarization resulting from mixing up of $2S_A$ and $2P_A$ orbitals, a typical component of which is given by

$$(\mu_{\text{hyb}})_x = -14.674 \sum_A^* \mathcal{G}_A^{-1} P_{2S_A, 2p_{xA}} \quad \text{Debye}$$

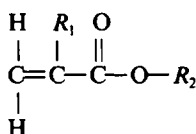
where \mathcal{G}_A is the orbital exponent of the valence orbitals of atom A . The asterisk implies that hydrogen atom is not included in the sum.

The most general molecular formula for these

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acrylate monomers chosen is



where R_1 and R_2 are the different substituent groups for different acrylates.

Methyl acrylate:	$R_1 = \text{H},$	$R_2 = \text{CH}_3$
Ethyl acrylate:	$R_1 = \text{H},$	$R_2 = \text{C}_2\text{H}_5$
Methyl methacrylate:	$R_1 = \text{CH}_3,$	$R_2 = \text{CH}_3$
Ethyl methacrylate:	$R_1 = \text{CH}_3,$	$R_2 = \text{C}_2\text{H}_5$

Standard bond angles and bond lengths (Table 1) are used for the initial geometry of a particular structure in a given system.⁴ The number following the symbol of the element denotes the connectivity of the atom. For e.g. C_3 denotes that carbon is bonded to 3 neighbours. If the connectivity is 4, tetrahedral angles are used. For connectivity 3, planar structure with bond angle 120° is used; atoms with connectivity 2 are taken as bent with a bond angle of 109.47° . The calculations are carried out on IBM 370/155 using CNDO/2 Force method (referred to as CNDO/F method). A brief account of CNDO method is given by Pople.⁴ A modified version of Pople's computer programme CNINDO is used in the present calculation to compute CNDO forces.

The optimization of the Geometry is done as described by Kanakavel *et al.*¹² For the proposed structures, in each system, the forces acting on all atoms in a system are calculated using an arbitrary geometry and CNDO wave functions. Each atom is then moved in the direction of the force acting on it, through a distance, say 0.01 \AA . With the new geometry thus generated, the forces are again computed and the nuclei allowed to relax towards the equilibrium geometry. This is repeated until consistency in energy and the minimum norm of the forces is obtained. This method is described as the "Steepest descent method".¹¹ The dipole moment corresponding to the lowest energy configuration (also minimum

norm of the force) is compared with the experimental value to arrive at the correct structure of the molecular system.

RESULTS AND DISCUSSION

On the basis of free rotation around C-C and C-O bonds, six different structures can be proposed and CNDO calculations on these conformers were carried out for methyl acrylate and it was found that two structures given in Figs. 1 and 2, are comparatively more stable in terms of the energy of the conformers. The calculated energies and dipole moments for the four acrylate monomers considered are given in Table 2 along with the reported experimental values. Out of the two structures studied in detail, the first structure leads to a lower energy value than the second in the case of methyl acrylate and ethyl acrylate whereas in the case of methyl metha and ethyl metha acrylates, second structure leads to a lower energy value. The difference in energy values of the two structures is of the order of 1.5 KCal/mole . Methyl methacrylate is obtained by replacing one hydrogen in the vinyl group by a Me group. This substitution leads to changes in charge relative to the parent molecule. There is a rearrangement of charge within the vinyl group mainly due to polarization rather than a net transfer of charge from methyl to vinyl group. This rearrangement trend was already observed in the case of simple molecules like ethylene and acetylene.⁴ The most significant change, however in such a redistribution process is that the Me group has driven away electrons from the atom to which it is attached onto the β C atom. For example in methyl acrylate-I the charge densities of α and β C atoms are

$$\begin{array}{rcl} +0.0328 & -0.0524 & = (\text{double bond}) \\ C_\beta & = & C_\alpha. \end{array}$$

While the corresponding distribution in methyl metha acrylate-I is

$$\begin{array}{rcl} +0.0051 & -0.0057 & \\ C_\beta & = & C_\alpha. \end{array}$$

(The figures are given in electrons.)

Another important result emerged on doing the Mulliken population analysis¹³ is that there is a small donation of π electrons from methyl to vinyl; nevertheless the main effect is a redistribution within the vinyl group. For example, again in methyl acrylate-I, the vinyl carbons have the following π electron distribution

$$\begin{array}{rcl} 1.2726 & 1.3067 & \\ C_\beta & = & C_\alpha \end{array}$$

while the corresponding figures in methyl metha acrylate-I are

$$\begin{array}{rcl} 1.2655 & 1.3381 & \\ C_\beta & = & C_\alpha. \end{array}$$

Pople⁴ has reported that substitution by methyl group in acetylene and ethylene resulted in donation of π electrons from methyl to vinyl, but β -carbon always acquired more electron density. But in our case, π electron density of β -C decreases on substitution by

Table 1. Bond lengths

Bond		Length in \AA
C-H	..	1.08
$\text{C}_3=\text{C}_3$..	1.34
C_3-C_3	..	1.46
C_3-C_4	..	1.52
C_3-O_2	..	1.36
C_3-O_1	..	1.22
C_4-O_2	..	1.43

Table 2. Results of CNDO calculation

MOLECULAR PROPERTIES	METHYL ACRYLATE CALCULATED			ETHYL ACRYLATE CALCULATED			METHYL METHACRYLATE CALCULATED			ETHYL METHACRYLATE CALCULATED		
	I	II	EXPERI- MENTAL	I	II	EXPERI- MENTAL	I	II	EXPERI- MENTAL	I	II	EXPERI- MENTAL

DIPOLE MOMENT IN DEBYES	1.57	1.66	1.59	1.54	1.73	1.65-1.67	1.68	1.72	1.66-1.68	1.68	1.78	1.72-1.82
	I	II	II	I	I	II	I	I	II	I	I	II

TOTAL ENERGY IN A.U.	-69.69031069	-69.69027015	-78.38814351	-78.38792115	-78.39582065	-78.398078483	-87.0934982633	-87.095703246	-----			

BINDING ENERGY IN A.U.	-5.03402298	-5.03398243	-6.28940168	-6.28917932	-6.29707882	-6.299336653	-7.5523023145	-7.5545072972	-----			

NORM. OF THE FORCE	0.022436	0.0144086	0.0149984	0.0147476	0.0161238	0.0167188	0.0148700	0.0147885	-----			

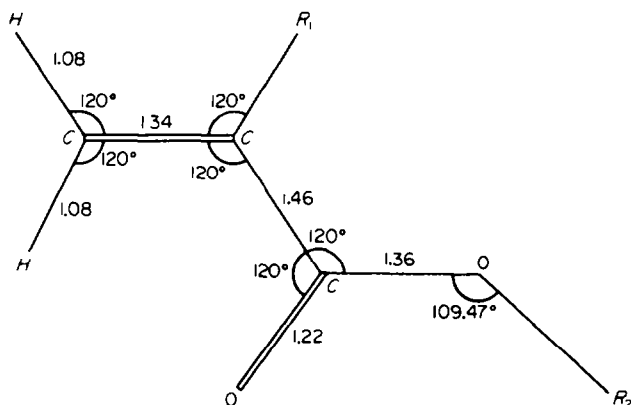


Fig. 1. Except R_1 and R_2 , all the atoms are in the plane of the paper.

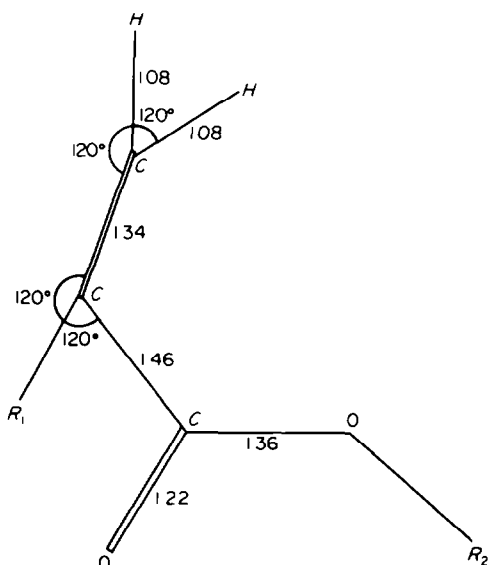


Fig. 2. Allyl group atoms are in the plane perpendicular to the plane of the paper.

Me group. This feature may be due to the presence of carboxyl group close to the α -C atom. Owing to its greater electronegativity, the carboxyl group would have attracted more electrons thus increasing the π electron density of α -carbon.

Another important feature noticed is that substitution by Me group lowers the total energy of the molecular system thus leading to better stability. This trend is reflected in the results of methyl acrylate and methyl methacrylate on one hand and ethyl acrylate and ethyl methacrylate on the other. Also substitution of Et group leads to a greater stability than the Me group substitution. This is seen from the results of methyl acrylate and ethyl acrylate. Dipole moment of the molecular system increases on substitution by Me group or Et group. This is because, there is a little overall charge transfer into vinyl group on substitution, but again the redistribution of charges between the α and β C's predominantly affects the dipole moment. This redistribution of charges is mainly associated with the π orbital electrons as reported by Pople⁴ in ethylene and acetylene.

Despite the approximation involved in CNDO calculations, it is observed that the calculated dipole moment values for the two conformers are comparable with the experimental values within the limits of accuracy of experimental results and theoretical calculations. For comparison sake however, it can be pointed out that experimental values for methyl acrylate and methyl methacrylate are closer to the theoretical values for conformer I whereas for ethyl acrylate and ethyl methacrylate the experimental values lie between the theoretical values of the two conformers. These observations lead to conclusion that most probably methyl acrylate and methyl methacrylate exist as conformer I whereas ethyl acrylate and ethyl methacrylate contain two conformers existing at equilibrium under the experimental conditions of temperature and solvent environment. A survey of theoretical values of dipole moments shows that even though the energy differences between the two conformers considered for the four acrylates are very small, the dipole moments for the II conformer is in general higher than that for the I conformer. Further studies on the effect of environment due to polarity of the solvent and variation in temperature on the dipole moments of these systems are in progress which will help in determining the possibilities of equilibrium between the two conformers under experimental conditions.

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REFERENCES

- ¹R. K. Khanna and J. Sobhanadri, *J. Phys. D: Appl. Phys.* **5**, 1453 (1972).
- ²R. K. Khanna and J. Sobhanadri, *Ibid.* **6**, 60 (1973).
- ³K. Higasi, *Bull. Chem. Soc. Japan* **39**, 2157 (1966).
- ⁴J. Delbene and H. H. Jaffe, *J. Chem. Phys.* **48**, 1807 (1968) and **50**, 563 (1968).
- ⁵J. A. Pople and G. A. Segal, *Ibid.* **44**, 3289 (1966).
- ⁶J. A. Pople, D. L. Beveridge and P. A. Dobosh, *Ibid.* **47**, 2026 (1967).
- ⁷J. A. Pople and D. L. Beveridge, *Approximate Molecular Orbital Theory*. McGraw-Hill, New York (1970).
- ⁸J. M. Sichel and M. A. Whitehead, *Theoret. Chim. Acta Berl.* **11**, 254 (1968).

- ⁹Roy Bruns and Willis B. Person, *J. Chem. Phys.* **55**, No. 11, (Dec. 1971).
- ¹⁰Roy Bruns and Willis B. Person, *J. Chem. Phys.* **58**, No. 6, (March 1973).
- ¹¹P. Pulay, *Mol. Phys.* **17**, 197 (1969).
- ¹²M. Kanagavel, J. Chandrasekhar, S. Subramanian and S. Singh, *Theoret. Chem. Acta Berl*, **43**, 185 (1976).
- ¹³R. S. Mulliken, *J. Chem. Phys.* **23**, 1833, 1841 (1955) and **36**, 3438 (1962).
- ¹⁴L. Onsager, *J. Am. Chem. Soc.* **58**, 1468 (1936).
- ¹⁵D. K. Deshpande and K. S. Rao, *Ind. J. Pure and Appl. Phys.* **7**, 439 (1969).