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ELECTRIC DIPOLEMOMENT OF AMYL CINNAMATE, AMYL PHENYLACETATE, PHENYL PROPYL BUTYRATE, GERANYL FORMATE AND GLYCERYL TRIACETATE

B. KRISHNA, S. C. SRIVASTAVA* and S. V. MAHADANE
Department of Physical Chemistry, University of Allahabad, Allahabad, India

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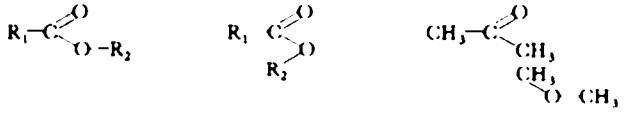
Abstract Electric dipolemoments of amylcinnamate, amyl phenylacetate, phenyl propylbutyrate, geranyl formate and glyceryl triacetate have been determined in benzene solution at a frequency of 1 Mc/s. The observed values of dipolemoments indicate the existence a *cis*- configuration in geranyl formate and a *trans*- configuration in amyl cinnamate, amyl phenylacetate and phenyl propylbutyrate, in which the C–O C plane lies considerably out of the *trans*- plane.

INTRODUCTION

IT HAS been pointed out[1,2] that the observed values for electric dipolemoments of monocarboxylic esters suggest that the actual structure of the ester corresponds to *trans*- (see I) Fig. 1 rather than *cis*- configuration (see II) Fig. 1. As a result of the monocarboxylic acid esters studied, it would be more reasonable to assume the existence of a *cis*- configuration or a *trans*- configuration in which the C–O–C plane has appreciably out of the *trans*- plane.



I II III

FIG. 1.

EXPERIMENTAL

The measurements were carried out at a frequency of 1 Mc/s. The apparatus employed is based on the hetro dyne beat method described.[4,5] The exact resonance point was obtained by means of a cathode ray tube which was used to observe Lissajous figures produced by beat frequency and 50 c/s mains frequency. The density of the solns has been determined with the help of pyknometer described.[6] The last traces of moisture in amyl cinnamate (Naarden, Holland), amyl phenylacetate (Haarmann & Reimer, Germany), phenyl propyl butyrate (Huizen, Holland), geranyl formate (Dubendorf Suisse, Switzerland) and glyeryl triacetate B.D.H.(L.R.) Poole, England) were removed by distillation and the fractions b.p. 192°/29 mm,

* Present address is Department of Physics, University of Allahabad, Allahabad.

[1] Eucken and Meyer, *Phys. Z.* **30**, 397 (1929).
[2] Marsden and Sutton, *J. Chem. Soc.* 1383 (1936).
[3] Table of Dipolemoments.
[4] B. Krishna and K. K. Srivastava, *J. Chem. Phys.* **27**, 835 (1957).
[5] B. Krishna and K. K. Srivastava, *J. Chem. Phys.* **32**, 663 (1960).
[6] S. C. Srivastava, *Dipolemoment and molecular structure*, doctoral thesis, Allahabad University (1964).

249° 250°, 210° 211°, 113° 114°/15 mm, 258° 259° respectively were collected and used. Benzene (A.R.; B.D.H. grade) was distilled in a quick fit apparatus and fraction b.p. at 78·5–79·5° was collected.

The polarization at infinite dilution was calculated with the help of Helverstadt and Kumler[7] Eq. in the form:

$$P_{2\infty} = \frac{3M_1\alpha v_1}{(\epsilon_1 + 2)^2} + (M_1\beta + M_2 v_1)\frac{(\epsilon_1 - 1)}{(\epsilon_1 + 2)} \tag{1}$$

where M_1 and M_2 are the mol. wt. of solvent and solute respectively, α and β are defined by the expression,

$$\epsilon_{12} = \epsilon_1 + \alpha f_2 \tag{2}$$

and

$$v_{12} = v_1 + \beta f_2 \tag{3}$$

where f_2 represents the mole fraction of the solute; ϵ_1, v_1 are the dielectric constant and molar volume of the solvent and ϵ_{12} and v_{12} are the dielectric constant and molar volume of the soln. The values of α, β, ϵ_1

TABLE 1. AMYL CINNAMATE IN BENZENE (Temp 25°)

S. No.	f_2	ϵ_{12}	v_{12}
1	0·00000	2·2791	1·145
2	0·00436	2·3048	1·143
3	0·00856	2·3205	1·142
4	0·01726	2·3875	1·138
5	0·03356	2·4850	1·111
6	0·04255	2·5370	1·109
7	0·04948	2·5750	1·106

α = 6·061 M_1 = 78·11
β = −0·4207 M_2 = 218·28
ϵ_1 = 2·279 P_e = 69·094
v_1 = 1·146 $P_{2\infty}$ = 153·83
$\mu = 2{\cdot}11 \times 10^{-18}$ e.s.u.

TABLE 2. AMYLPHENYLACETATE IN BENZENE (Temp 25°)

S. No.	f_2	ϵ_{12}	v_{12}
1	0·00000	2·2690	1·144
2	0·00445	2·2978	1·143
3	0·00916	2·3295	1·142
4	0·01797	2·3764	1·139
5	0·01820	2·3650	1·138
6	0·04236	2·4980	1·132
7	0·05137	2·5310	1·130

α = 6·181 M_1 = 78·11
β = −0·1944 M_2 = 206·27
ϵ_1 = 2·270 P_e = 64·924
v_1 = 1·144 $P_{2\infty}$ = 156·11
$\mu = 2{\cdot}13 \times 10^{-18}$ e.s.u.

[7] I. F. Halverstadt and W. T. Kumler, *J. Am. Chem. Soc.* **63**, 2988 (1942).

TABLE 3. PHENYL PROPYL BUTYRATE IN BENZENE (Temp. 25°)

S. No.	f_2	ϵ_{12}	v_{12}
1	0·00000	2·2784	1·144
2	0·00461	2·3002	1·143
3	0·00954	2·3134	1·139
4	0·01936	2·3821	1·135
5	0·02885	2·4740	1·132
6	0·03689	2·4960	1·128
7	0·04753	2·5520	1·123
8	0·05705	2·6270	1·119

α = 6·210 M_1 = 78·11
β = −0·4245 M_2 = 206·27
ϵ_1 = 2·273 P_e = 64·924
v_1 = 1·144 $P_{2\infty}$ = 151·58
$\mu = 2{\cdot}06 \times 10^{-18}$ e.s.u.

TABLE 4. GERANYL FORMATE IN BENZENE (Temp 25°)

S. No.	f_2	ϵ_{12}	v_{12}
1	0·00000	2·2704	1·145
2	0·00497	2·3095	1·144
3	0·01048	2·3657	1·143
4	0·01868	2·3995	1·142
5	0·02001	2·4576	1·141
6	0·02514	2·5060	1·139
7	0·02956	2·5540	1·138
8	0·03543	2·5850	1·137

α = 9·245 M_1 = 78·11
β = −0·2161 M_2 = 182·25
ϵ_1 = 2·267 P_e = 53·980
v_1 = 1·148 $P_{2\infty}$ = 189·22
$\mu = 2{\cdot}57 \times 10^{-18}$ e.s.u.

TABLE 5. GLYCERYLTRIACETATE IN BENZENE (Temp 25°)

S. No.	f_2	ϵ_{12}	v_{12}
1	0·00000	2·2760	1·145
2	0·00522	2·3446	1·142
3	0·01012	2·3834	1·138
4	0·01506	2·4378	1·134
5	0·01982	2·4950	1·130
6	0·03442	2·5680	1·124
7	0·03809	2·6490	1·120
8	0·04393	2·7340	1·114

α = 9·493 M_1 = 78·11
β = −0·6510 M_2 = 218·20
ϵ_1 = 2·286 P_e = 49·144
v_1 = 1·144 $P_{2\infty}$ = 201·63
$\mu = 2{\cdot}73 \times 10^{-18}$ e.s.u.

and v_1 have been determined by the method of least squares.[8] The method of calculation has been described earlier.[9]

DISCUSSION

As pointed out,[2] provided there is no interaction between the ether and the carboxyl groups, the moment of methyl acetate should be equal to the resultant of the moments of dimethyl ether and acetone inclined at an angle ϕ determined by the configuration (see II) Fig. 1, 180° for the *trans*- and 70·5° for the *cis*. Calculated values for the *trans*- and *cis*- configuration are respectively 1·53 and 3·53 D respectively. The experimentally observed value for the methyl acetate vapour[3] is 1·67 D, so that the actual structure closely corresponds to a *trans*- configuration. Accordingly,[2] most of the observed values of the moments for the esters vary roughly from 1·7 to 1·9 D—the deviation from the calculated value for the *trans*- configuration (1·53 D) being due to existence of induction and wave-mechanical resonance between the classical structure (IV) Fig. 2 with an excited one (V) Fig. 2.

FIG. 2.

Here we shall not discuss the case of glyceryl triacetate (2·73 D) which is a derivative of trihydric alcohol and contains three carboxylate groups. In case of other esters (amyl cinnamate, amyl phenylacetate, phenyl propyl butyrate and geranyl formate), our measurements show that the actual values for the moments vary from 2·06–2·57 D. These observed values are much greater than expected on simple theoretical grounds for the *trans*- configuration (1·53 D). In the latter case, one has to assume a large contribution from the excited structures. There seems, however, no reason why such excited structures should contribute more for the present esters than for previously studied esters (e.g. methyl-acetate) which give notably smaller experimental moments and closer to the theoretically expected value of 1·5 D or thereabouts. In case of geranyl formate (2·75 D) the data obtained definitely points to a *cis*-structure while in others (amyl cinnamate, amyl phenylacetate and phenyl propyl butyrate), one may assume the existence of a *trans*- configuration in which the C–O–C plane lies considerably out of the *trans*- plane.

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[8] J. W. Mellor, *Higher Mathematics for students of Chemistry and Physics* pp. 326. Dover, New York (1954).
[9] B. Krishna, B. B. L. Saxena and S. C. Srivastava, *Tetrahedron* **22**, 1597 (1966).