Dipole Moments of Some Cyclic Anhydrides

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New values of the dipole moments of maleic anhydride and three of its Diels-Alder adducts have been determined using the technique of Guggenheim. The results are compared with the dipole moments of several other cyclic anhydrides.

The dipole moment of a molecule not only provides valuable structural information but also is essential for the interpretation of intermolecular interactions in solution. Maleic anhydride has frequently been used as a dienophile for several investigations on Diels-Alder reactions (*2, 7, 9*). In this work, we report new values for the dipole moment of maleic anhydride and for three of its Diels-Alder adducts, all in benzene at 25° C. Determinations were made by measurements of the dielectric constants and refractive indices of dilute solutions of the anhydrides in benzene.

EXPERIMENTAL

Eastman reagent maleic anhydride was vacuum sublimed. Eastman practical grade *cis*-4-cyclohexene-1,2-dicarboxylic anhydride (CDA—the adduct of maleic anhydride with 1,3-butadiene) was recrystallized from anhydrous ethyl ether, mp = 102–103.5° C. The 4-methyl-(MCDA) and 3-methoxy-(MOCDA) derivatives of CDA were prepared by the Diels-Alder addition to maleic anhydride of isoprene and 1-methoxy-1,3-butadiene, respectively, and subsequent purification by recrystallization, as described by Grieger (*5*). All anhydrides were stored and loaded into solution in a dry box. The solvent used was Baker thiophene-free spetrophotometric benzene, dried before use with Linde 4A molecular sieves.

Dielectric constant measurements were made using a highly accurate heterodyne beat technique, which compares the frequency of a fixed crystal-controlled reference oscillator with that of a variable oscillator. The precision measuring capacitor was a General Radio 722-D variable air capacitor which was calibrated by the Betatron Laboratory at the University of Illinois. The capacitor could be read directly to ±0.1 pF and estimated to ±0.02 pF. The electronics were grounded and thermally insulated. Coaxial cables were used and connected with UHF connectors. Further details of the apparatus are given elsewhere (*4, 10*).

The dielectric cell was a brass cylinder with a flanged top containing a carefully machined (±0.0002 in.) capacitor. The latter consisted of concentric brass cylinders, insulated and held in place by rigid alumina support rings. The working dielectric gap was 0.3008 in. i.d. and 0.3550 in. o.d. and about two inches long. The entire dielectric cell was immersed in a water bath maintained at 25.00 ± 0.01° C, as measured by a thermometer which was calibrated against a NBS certified thermometer. The dielectric cell was calibrated at 25.00° C with three highly purified materials of known dielectric constant—*n*-butyl ether, chlorobenzene, and 1,2-dichloromethane.

For each run, the dielectric cell was cleaned, thoroughly dried, and filled carefully to avoid bubbles. Then the change in cell capacitance, relative to the capacitance for dry nitrogen, was measured for the pure solvent benzene and for a series of dilute solutions of each anhydride. A series of readings, always reproducible to better than ±0.05 pF (0.1%) were taken for each solution. Also for each solution the refractive index at 25° C was measured to ±0.0001 with a Spencer Abbé-type refractometer (American Optical Co.).

RESULTS AND DISCUSSION

Although the dipole moment can be obtained from other sources, such as from the Stark effect in microwave spectra, dielectric constant data are frequently used. In general, the theories of polarization of Debye or Onsager have been used. Guggenheim (*6*) suggested a simplified computational procedure based on the Mosotti-Clausius-Debye treatment, whereby the dipole moment, μ is given by:

$$\mu^2 = (27\,kT/4\,\pi N)[M_2/\rho_1(\epsilon_1 + 2)^2](a_\epsilon - a_n) \tag{1}$$

where k is the Boltzmann constant, N is the Avogadro's number, M_2 is the molecular weight of the solute, ρ_1 and ϵ_1 are the density and dielectric constant of the solvent, a_ϵ and a_n are the slopes of ϵ and n_D^2 vs. weight fraction of the solute at infinite dilution, and n_D is the refractive index of the solution of the sodium-D line.

Guggenheim's method eliminates some of the difficulties in the usual procedure for determining the electric dipole moment of a polar solute in a nonpolar solvent. Equation 1 assumes that atomic polarizations are proportional to molar volumes, and also that n_D may be substituted for the infinite-wavelength extrapolation of the refractive index. The advantages of this technique include the fact that data at only one temperature are required, and no density other than that of the pure solvent is needed. The dielectric constant data and refractive index data may be extrapolated separately to infinite dilution; moreover, both are linear in weight fraction and thus give excellent values of the slopes, a_ϵ and a_n. An example of such an extrapolation is shown in Figure 1. For the polar molecules studied here, the contribution of a_n is nearly negligible, for example 0.5% only for MOCDA.

Table I. Dipole Moment of Some Cyclic Anhydrides

	μ, *D*	Temp, ° C	Solvent
Maleic anhydride	3.95	25	Benzene
	3.94	35	Dioxane[b]
	3.92[a]	25	Benzene[c]
CDA	4.53	25	Benzene
MCDA	4.46	25	Benzene
MOCDA	5.25	25	Benzene
Citraconic anhydride	4.26	10	Benzene[b]
Succinic anhydride	3.83	25	Benzene[b]
Phthalic anhydride	5.29	10-40	Benzene[b]

[a] Extrapolated value at infinite dilution from data of Crump and Price (*3*). [b] McClellan, (*8*). [c] Crump (*3*).

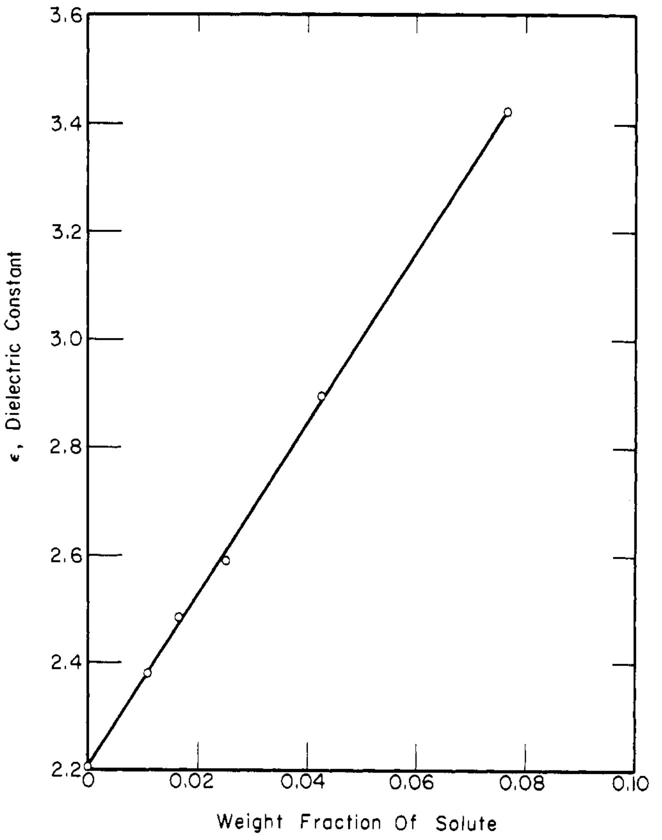

Figure 1. Dielectric constant of 3-methoxy-*cis*-4-cyclohexene-1,2-dicarboxylic anhydride in benzene at 25.00° C

The observed dipole moments in benzene at 25° C are presented in Table I along with the reported dipole moments of three other cyclic anhydrides (*8*). The value found for maleic anhydride agrees to 0.03*D* (0.8%) with the infinite dilution extrapolation of data in benzene at 25° C (*3*), and is within 0.01*D* of the value found in dioxane at 35° C (*8*).

From a comparison of the dipole moments of citraconic and succinic anhydrides with that for maleic anhydride, it appears that the methyl group at the double bond increases μ while the loss of the unsaturation decreases it. However, if the double bond is not conjugated, as in CDA, then a methyl group (MCDA) changes μ only very slightly. On the other hand, a methoxy group (MOCDA) increases μ dramatically, since the group moment contribution for the CH_3O-group is 1.22*D* (*11*) and the cyclohexene configuration is nonplanar. Greater unsaturation in the six-member ring, including conjugation with the carboxyl groups, in phthalic anhydride, gives a significantly higher μ than for CDA.

Recently the dipole moments of the two isomeric Diels-Alder bicyclo-adducts of cyclopentadiene to maleic anhydride have been measured in two solvents (*1*). The authors report for the *exo* and *endo* forms respectively, $\mu_X = 3.91D$ and $\mu_N = 4.32D$ in carbon tetrachloride, and μ_X 4.32*D* and $\mu_N = 4.46D$ in dioxane.

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RECEIVED for review March 16, 1970. Accepted August 14, 1970. The financial support of the U.S. Army Research Office-Durham is gratefully acknowledged.

Diffusion Coefficients of Ethylene Glycol and Cyclohexanol in the Solvents Ethylene Glycol, Diethylene Glycol, and Propylene Glycol as a Function of Temperature

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The binary molecular diffusion coefficients of the solutes ethylene glycol and cyclohexanol in the solvents ethylene glycol, diethylene glycol, and propylene glycol at various temperatures ranging from 25° to 50° C were measured in this work. This investigation extends the data previously obtained in this laboratory (*6*) at 30° C. The importance of these diffusivities is twofold. First, they are useful as experimental data in themselves, and second, they can be used to test theories developed for estimating binary diffusion coefficients. For this second application, these data cover a range of solvent viscosities where there is a noticeable lack of experimental data—namely, about 7 to 43 centipoises. The self-diffusion coefficient of ethylene glycol was also determined as a function of temperature.

A modified absolute rate theory equation developed earlier in this laboratory (*6*) is used to estimate these diffusion coefficients. Also, the ability of this equation to account adequately for the effect of temperature is examined, with activation enthalpies of diffusion being calculated.

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