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Identification of Stereoisomers Based on Dielectric Studies: Dipole Moments of Chloroalkenes and Chlorocumulenes

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Summary: The use of dielectric measurements to assign molecular configurations was examined with model compounds of the chloroalkane, chloroalkene and chlorocumulene type. A dielectric microcell is described which allows measurements of 0.35 mL samples under exclusion of air. Both benzene and cyclohexane were used as solvents. Different theories of dielectric constant are compared to evaluate dipole moments. Dipole moments are analyzed in terms of bond moments. - The results can be summarized as follows: (i) dielectric measurements are feasible up to 1 M solutions without substantial deviation from linearity; (ii) in general, the dipole moments found in both solvents are similar; the aromatic solvent, however, causes a substantial decrease of the values obtained for chloroalkenes with two bulky substituents at the double bonds; (iii) the (*E*) isomers of chloroalkenes exhibit significantly higher dipole moments than the corresponding (*Z*) isomers; (iv) isomers of non-chlorinated alkenes or cumulenes with dipole moments below 0.6 D cannot be discriminated dielectrically; (v) on the other hand, if the dipole moments of the compounds exceed 1 D, configurations can be assigned unambiguously on the basis of. dielectrical data even in cases where other approaches fail.

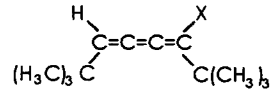
In general, the assignment of (*Z*) or (*E*) configurations to 1,2-disubstituted ethylenes is trivial. In most cases the $^3J_{HH}$ coupling constants will procure an unequivocal answer. Difficult problems may be solved by double irradiation of neighbouring nuclei [1], through-space magnetization transfer (Overhauser effect measurement) or ^{13}C chemical shifts. The latter method is also very valuable for the configurational assignment of alkenes belonging to the trisubstituted ethylene type.

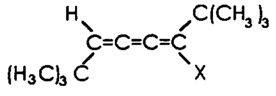
Nuclear magnetic resonance (nmr) techniques can again be successfully applied to 1,3-butadienes but they fail with 1,2,3-butatrienes. Though strong, $^5J_{HH}$ long-range couplings do not provide any reliable spatial information [2]. For example, almost identical $^5J_{HH}$ values were recorded with (*Z*)- and (*E*)-2,2,7,7-tetramethyl-3,4,5-octatriene (*Z*- and *E*-**1**, "*cis*- and *trans*-1,4-di-*tert*-butyl-1,2,3-butatriene") [3].

The purpose of this article is to draw attention to a classical method which has unjustly fallen into oblivion. Dipole moment measurements [4] continue to constitute a major and very powerful tool for structure elucidation. Recent instrumental progress [5] makes this method even more attractive since no longer unreasonably large quantities of material are required.

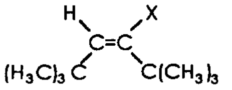
Configuration assignment

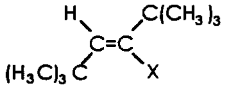
We have determined the dipole moments of three simple, saturated or unsaturated chlorohydrocarbons (neopentyl chloride (**2**), 2-chloro-1-butene (**3**) and 2-chloro-3,3-dimethyl-1-butene (**4**)), three pairs of (*Z*) and (*E*) stereoisomeric chloroalkenes (1-chloro-1-butenes (**5**), 1-chloro-3,3-dimethyl-1-butenes (**6**) and 3-chloro-2,2,5,5-tetramethyl-3-hexenes (**7**)) and, finally, a (*Z*) and (*E*) pair of a chlorocumulene (3-chloro-2,2,7,7-tetramethyl-3,4,5-octatriene (**8**)).





X = H	**Z-1**	**E-1**
X = Cl	**E-8**	**Z-8**





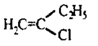
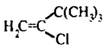
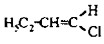
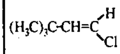
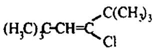
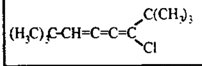
X = H	**Z-9**	**E-9**
X = Cl	**E-7**	**Z-7**

As Table 1 shows, the (*E*)-isomers have invariably higher increments of dielectric constants (and hence, dipole moments) than the (*Z*)-isomers. The difference in the dipole moments of the (*E*)- and (*Z*)-stereoisomers was 0.3 - 0.4 D for the *tert*-butyl derivatives, and 0.2 D for the ethyl derivatives. For the cumulenes, the differences of the increments of dielectric constant between the (*E*)- and the (*Z*)-isomers were particularly pronounced (Fig. 1). Consequently, the differences in the dipole moments of these isomers were large, being 0.37 D and 0.61 D in benzene and cyclohexane, respectively. Such differences allow an unambiguous assignment in every case.

Evaluation of Dipole Moments

Dipole moments were calculated based on Debye's and Onsager's theory of dielectric constants (*see* Procedures and Evaluation). The dipole moments obtained from different theories and methods vary at most by about 0.07 D (Table 2). In particular, the dipole moments evaluated by method B3 (Fig. 2) are virtually identical with the values obtained by method B2 (least square sum method).

Table 1. Increments of dielectric constant and dipole moments.

model compound	cpd. no.	config.	increment of dielectric constant (L/mol) in solvent: C_6H_{12} / C_6H_6	dipole moment (D) in solvent: C_6H_{12} / C_6H_6
$(H_3C)_3C-CH_2-Cl$	2	-	0.468 / 0.436	2.0 / 2.0
 $H_2C=C(C_2H_5)Cl$	3	-	0.359 / 0.296	1.7 / 1.6
 $H_2C=C(C(CH_3)_3)Cl$	4	-	0.360 / 0.277	1.8 / 1.6
 $H_5C_2-CH=C(H)Cl$	5	(*Z*) (*E*)	0.306 / 0.291 0.392 / 0.385	1.6 / 1.6 1.8 / 1.8
 $(H_3C)_3C-CH=C(H)Cl$	6	(*Z*) (*E*)	0.228 / 0.239 0.365 / 0.419	1.4 / 1.5 1.8 / 1.9
 $(H_3C)_3C-CH=C(C(CH_3)_3)Cl$	7	(*Z*) (*E*)	0.488 / 0.263 0.674 / 0.582	2.0 / 1.6 2.3 / 2.2
 $(H_3C)_3C-CH=C=C=C(C(CH_3)_3)Cl$	8	(*Z*) (*E*)	0.424 / 0.333 0.763 / 0.530	1.7 / 1.6 2.3 / 2.0

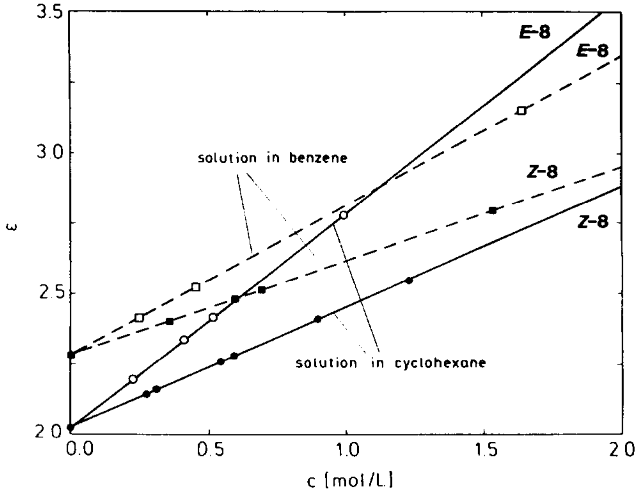


Fig. 1: Dielectric constant of 1-chloro-1,4-di-*tert*-butyl-1,2,3-butatriene in benzene (squares) and cyclohexane (circles). Filled symbols: (*Z*) isomer; open symbols: (*E*) isomer.

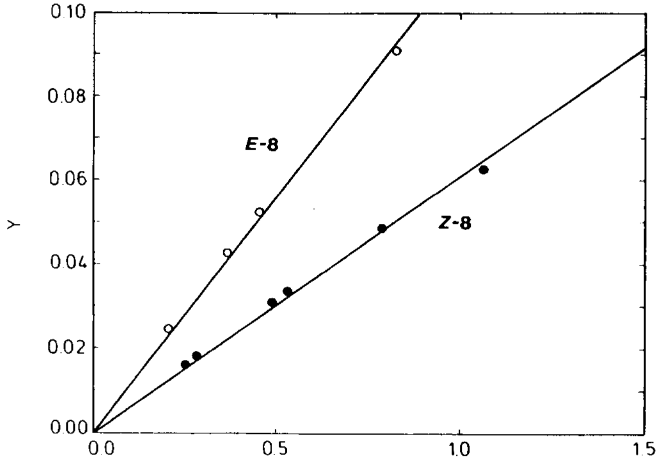


Fig. 2: Plot of the x and y terms as defined by eq. (6a,b) for 1-chloro-1,4-di-*tert*-butyl-1,2,3-butatriene in cyclohexane. Filled circles: (*Z*) isomer; open circles: (*E*) isomer.

The extension of dielectric measurements to the concentration range above 1 M solutions might appear unreasonable. However, the deviation of the dielectric constant from linearity is amazingly small, as shown in Fig. 3. Even for the greatest dipole moment determined, it is not detectable within the experimental error limits of about ±1%. For smaller dipole moments, the deviation from linearity is accordingly smaller.

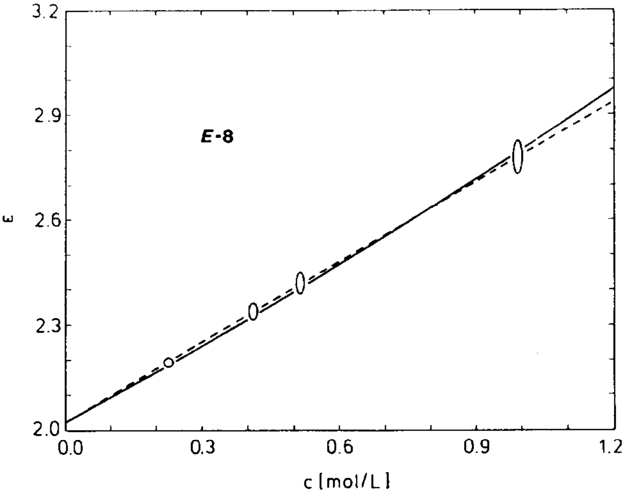


Fig. 3: (*E*)-1-chloro-1,4-di-*tert*-butyl-1,2,3-butatriene in cyclohexane: comparison of the dielectric constant, ε, as calculated from the Onsager equation, eq. 4 (solid line; μ = 2.33 D, density = 0.90 g/ml; 20 °C) with the linear regression (dashed line) through the experimental points, the latter being identical with those shown in Fig. 2.

Solvent Effects

Since benzene, the standard solvent for dielectric measurements, is more polarizable than cyclohexane one might expect the aromatic solvent to attenuate the polarity of the solute. However, the compounds **2**, **3**, **5** and **6** exhibit very similar, if not identical dipole moments in both solvents. On the other hand, the shift from the aliphatic to the aromatic solvent causes a substantial decrease of dipole moments with both isomers of 3-chloro-2,2,5,5-tetramethyl-3-hexene (**7**) and 3-chloro-2,2,7,7-tetramethyl-3,4,5-octotriene (**8**). The origin of this phenomenon may be a steric one. The two bulky *tert*-butyl groups may interfere more strongly with the disk-like benzene rather than the chair-shaped cyclohexane molecules and keep the former at a larger distance.

Non-chlorinated Hydrocarbons

Based on the vector addition model of individual bonds or group bonds, the difference of 0.3 D found between, say, (*Z*)- and (*E*)-3-chloro,2,2,5,5-tetramethyl-3-hexene should also hold for *trans*- and *cis*-2,2,5,5-tetramethyl-3-hexene (**9**, "di-*tert*-butylethylene"). The same should be true for the chlorocumulenes *Z*-**8** and *E*-**8** and their halogen-free counterparts *trans*-**1** and *cis*-**1**.

Of course, the dipole moments of both *trans* isomers of compounds 1 and 9 are zero; on the other hand, the *cis* isomers of these compounds should have finite dipole moments of about 0.3 D. However, the increments of the dielectric constants of all samples of 1 and 9, no matter whether *cis*- or *trans* isomers, turned out to be indistinguishable from zero within the experimental error of about 1%.

Bond Moments

Assuming that the total dipole moment of a compound is essentially given by the vector addition of the bond moments [4], the dipole moments of the C-Cl-bond and the (C_{sp^3})-(C_{sp^2})-bond were calculated. The values of the C-Cl bond moments were reasonably constant and agree well with the standard value 1.60 D for the C_{sp^2}-Cl bond reported for aromatic compounds [4]. The results for C-R bond moments are somewhat more variable but for similar compounds they agree within the combined inaccuracy of the experiments and of the additivity principle of bond moments.

Presumably, the bond moments are to some extent due to moments induced within the alkyl groups by the C-Cl bond. This follows from the smaller values for the ethyl derivatives (5) than for *tert*-butyl derivatives (6) and (7), while these should be equal on the basis of the pure bond moment scheme [4].

On the other hand, the polarization should decrease with increasing distance of the carbon-chlorine bond in the 3-chloro-2,2,7,7-tetramethyl-3,4,5-octatrienes (8). Nevertheless, we observe an enhanced difference in dipole moments of these stereoisomers. We attribute this finding to an electronic polarization of the double bond systems being interposed between the two dipoles, thereby amplifying the total charge separation. Similar effects had previously already been recognized with model compounds of the polyene type [5].

Limits of the Method

The difference in dipole moments might be supposed to be even more accentuated if the carbon-chlorine bond is eliminated and only the crucial variable of relative alkyl positions is maintained. However, the compounds 1 and 9 gave no measurable increase of the dielectric constant. What appears to be a paradox at first sight is easily understood as soon as one remembers that the dielectric constants, ε, correlate with the square roots of the dipole moments, μ; according to eq. (2), a test compound having a dipole moment of 0.6 D augments even in 1 M concentration the dielectric constant of the solution only by about 2%, just enough to be detected beyond doubt. It is, therefore, advisable that the difference of the total dipole moments of two isomers is about 1 D in order to discriminate safely between a more and a less polar isomer.

Conclusion

We have shown that even small differences of polarity are reliably detected if the total dipole moment of the compound is high enough, *i.e.* above at least 0.6 D. Alkyl groups can be represented as small dielectric vectors where hydrogen atoms act as the positive and carbon atoms as the negative pole; the difference of about 0.3 D is sufficient for a reliable assignment of the configuration of (*E*)- and (*Z*)-chlor-alkenes. Hence, dielectric measurements continue to constitute a valuable method to elucidate molecular structure. There are even cases [25] where this method cannot be replaced by nmr spectroscopy.

PROCEDURES AND EVALUATION

1. SAMPLES

The (*Z*) and (*E*) isomers of 1-chloro-1-butene [6] (***Z***- and ***E*-5**), n_D^{15} 1.4194 and 1.4225, respectively), 2-chloro-1-butene[6, 7] (**3**, n_D^{21} 1.4115), 2-chloro-3,3-dimethyl-1-butene [8] (**4** n_D^{20} 1.4251) and the (*Z*) and (*E*) isomers of 3-chloro-2,2,5,5-tetramethyl-3-hexene [9] (***Z***- and ***E*-7**, n_D^{20} 1.4448 and 1.4618, respectively) were prepared according to literature procedures. The (*Z*)- and (*E*)-isomers of 1-chloro-3,3-dimethyl-1-butene[10, 11] (*Z*- and *E*-**6**, n_D^{20} 1.4252 and 1.4280, respectively) were obtained as a 1 : 4 mixture by the Wittig reaction between pivalaldehyde and (triphenylphosphonio)chloromethanide [12] before being separated by preparative gas chromatography (6 m, 20 % silicon rubber SE-30, 120 °C).

3-Chloro-2,2,7,7-tetramethyl-3,4,5-octatriene (8): A solution of 2,2,7,7-tetramethyl-4-octyne-3,6-diol [13] (*meso* : *dl* ~ 1 : 1; 40 g, 0.20 mmol) and triphenylphosphine (158 g, 0.60 mol) in tetrachloromethane (0.40 L) was heated 3 h under reflux before being concentrated to half of its volume. Upon addition of pentane (0.40 L) a precipitate formed from which the supernatant liquid was decanted after centrifugation. The solvent was evaporated and the residue distilled to afford 40 g (83 %) of **3,6-dichloro-2,2,7,7-tetramethyl-4-octyne** (*meso* : *dl* ~ 1 : 1.2 [14]); bp 58 - 60 °C/0.2 mmHg; mp 10 - 15 °C; ^{1}H-NMR ($CDCl_3$, 80 MHz): δ 4.36 (2 H, s), 1.11 (18 H, s). - This product (35 g, 0.15 mol) was added to a precooled suspension of potassium *tert*-butoxide (18 g, 0.16 mol) in pentane (0.25 L) and the mixture was stirred for 3 days at -50 °C. The material collected after a first, crude distillation contained still some dichloride and some 2,2,7,7-tetramethyl-3,5-octadiyne [15] (approximately 15 % each). Careful spinning band distillation gave pure **8** having a (*Z/E*) ratio ranging from 1 : 2 to 1 : 3, bp 63.0 - 64.5 °C/0.2 mmHg. After addition of a trace amount of iodine and exposure to sunlight the isomeric composition approached 1 : 1.2 as evidenced by capillary gas chromatography (45 m Carbowax 20 M, 70 °C) and nmr (see below). The two isomers were separated by preparative gas chromatography (6 m 30 % diethyleneglycol succinate, or 6 m 20 % Carbowax 20 M, 120 → 135 °C, increasing the temperature at a rate of 3 °C/min, temperature of the detector exit 130 °C). ***Z*-8**: mp -8 to -6 °C; n_D^{20} 1.5159; ^{1}H-NMR ($CDCl_3$, 80 MHz) : δ 5.60 (1 H, s), 1.20 (9 H, s), 1.13 (9 H, s); Analysis: calc. for $C_{12}H_{19}Cl$ (198.74) C 72.52, H 9.64; found C 72.67, H 9.70 %. ***E*-8**: becomes glassy below -50 °C; n_D^{20} 1.5180; ^{1}H-NMR ($CDCl_3$, 80 MHz): δ 5.58 (1 H, s), 1.24 (9 H, s), 1.12 (9H, s); Analysis: calc. for $C_{12}H_{19}Cl$ (198.74) C 72.52, H 9.64; found C 72.43, H 9.64%.

2,2,7,7-Tetramethyl-3,4,5-octatriene (1): Under nitrogen, acid or copper activated zinc (6.5 g, 100 mmol) was added to a solution of 3,6-dichloro-2,2,7,7-tetramethyl-4-octyne (11.8 g, 50 mmol) in tetrahydrofuran (50 mL) and the mixture was heated to reflux for 15 h. Filtration and distillation gave 6.0 g (73 %) of a 3 : 1 mixture of *Z*-**1** and *E*-**1** which was still contaminated with a small amount (< 10 %) of (*Z*)- and (*E*)-4-chloro-2,2,7,7-tetramethyl-3-octen-5-yne (see below). The isomeric products were separated by preparative gas chromatography (6 m 20 % Carbowax 20 M, 120 °C). - (*E*)-**1**: mp 64 - 65 °C; ^{1}H-NMR ($CDCl_3$, 360 MHz): δ 5.50 (2 H, s), 1.08 (18 H, s); ^{1}H-NMR (C_6D_6, 360 MHz): d 5.54 (2 H, s) 1.08 (18 H, s); Analysis: calc. for $C_{12}H_{20}$ (164.29) C 87.73, H 12.27, found C 88.02, H 12.06 %. - (*Z*)-**1**: mp 21 - 23 °C; ^{1}H-NMR ($CDCl_3$, 80 MHz): δ 5.46 (2 H, s), 1.12 (18 H, s); ^{1}H-NMR (C_6D_6, 360 MHz): δ 5.53 (2 H, s), 1.08 (18 H, s).

(*Z*)- and (*E*)-**4-Chloro-2,2,7,7-tetramethyl-3-octen-5-yne** [16]: Analysis : calc. for $C_{12}H_{19}Cl$ (198.74) C 72.52, H 9.64, found C 72.41, H 9.57 %; ^{1}H-NMR ($CDCl_3$, 80 MHz) of the (*Z*)-isomer : δ 5.95 (1 H, s), 1.24 (9 H, s), 1.19 (9 H, s); ^{1}H-NMR ($CDCl_3$, 80 MHz) of the (*E*)-isomer: δ 5.93 (1 H, s), 1.27 (9 H, s), 1.18 (9 H, s). - Configurational assignment by comparison with (*Z*)- and (*E*)-**3-chloro-6,6-dimethyl-2-hepten-4-yne**; Analysis: calc. for $C_9H_{13}Cl$ (156.66) C 69.00, H 8.36, found C 68.90, H 8.41 %; ^{1}H-NMR ($CDCl_3$, 60 MHz) of the (*Z*) isomer: δ 6.03 (1 H, q, J 6), 1.79 (3 H, d, *J* 6), 1.25 (9 H, s); ^{1}H-NMR ($CDCl_3$, 60 MHz) of the (*E*) isomer; d 6.00 (1 H, q, *J* 6), 1.81 (3 H, d, *J* 6), 1.28 (9 H, s).

2. DIELECTRIC MEASUREMENTS

Since the chlorocumulenes **8** are fairly air sensitive, a small dielectric cell has been constructed such as to avoid any air contact of the sample during filling and measurement. As shown in Fig. 4, the cell has cylindrical shape and a void volume of 0.35 mL; the void capacity was 3.5 pF. Its central part is 15 mm long, consisting of an inner electrode of 3 mm in diameter and an outer electrode of 7 mm diameter. The cell is covered on both sides with 2 mm thick glass rings which are sealed with a solvent resistant epoxide resin (Ciba-Geigy components AW 139 and HV 998 mixed in a 15:8 w/w ratio). A light conductor was mounted onto the transparent cell to enable visual control of proper filling of the cell. Two cannulas sealed to one side of the dielectric cell (labelled f and g in Figure 4) served as inlet and outlet which were fitted to silicon tubes stoppered with small glass rods. The temperature of the cell was kept constant at 20 ± 0.01 °C throughout all measurements.

Prior to use, the dielectric cell was thoroughly flushed with argon. The solution was then transferred to the cell through the inlet cannula by means of a 500 μL Hamilton glass syringe while the outlet was connected to an argon purged balloon. Capacity measurements were carried out at different frequencies (30 kHz, 100 kHz, 300 kHz, or 10 kHz, 30 kHz, 50 kHz) using a Boonton 75 C capacity bridge. The cell was calibrated with air, hexane, cyclohexane, benzene, dioxane, and chloroform. Blank or sample measurements were found to be reproducible within ± 1% limits.

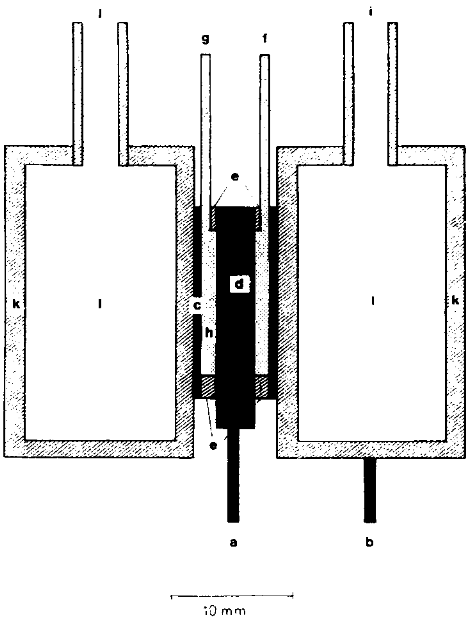


Fig. 4. Cross section of the cylindrical dielectric cell. a) electric connection to inner electrode (brass); b) electric connection to outer electrode (brass); c) outer electrode (platinum); d) inner electrode (platinum); e) glass rings (insulators); f) inlet cannula; g) outlet cannula; h) sample volume; i, j) connections to the thermostat; k) thermostat mantle (brass); l) thermostatted chamber.

3. COMPUTATIONAL EVALUATION

Dipole moments were calculated based on both Debye's [17] and Onsager's [18] theories of dielectric constant.

Method A: although the concentrations used are 10 times higher than commonly used [19, 20] (but comparable to those used in the classical work of LeFèvre [21]) the classical Halverstadt-Kumler equation [22] - which is based on Debye's theory - was found to be applicable. In this equation, the dipole moment, μ, of the solute (in Debye units, D; in international units, 1D equals $3.334 \cdot 10^{-30}$ Cm) is given by

$$\mu = \sqrt{\frac{9kTM_2}{4\pi N}\left(\frac{3\alpha}{d_1(\varepsilon+2)^2} + \frac{\varepsilon-1}{\varepsilon+2}\cdot\frac{1}{d_2} - 1.05\cdot\frac{n_2^2-1}{n_2^2+2}\cdot\frac{1}{d_2}\right)} \qquad (1)$$

In this equation, index 1 denotes the solvent,and index 2 the solute, N stands for Avogadro's number and k for Boltzmann's constant, M_2, n_2 and d_2 denote the molar mass, the refractive index and the density of the solute, respectively; T denotes the absolute temperature (in Kelvin), and ε the dielectric constant. After recalculating the concentrations c into weight fractions, w, the plot of ε *vs.* w is reasonably linear, yielding for w → 0 the value of $\alpha = \lim(\delta\varepsilon / \delta w)$. Eq. (1) differs from the original form [22] only in the direct use of the solute density d_2 instead of the value obtained indirectly from solution measurements.

Method B1-B3. The Onsager theory provides a more rigorous treatment of dielectric constants because it takes into account the polarizability of the solute. For a two component system of a polar solute dissolved in a non-polar solvent, the Onsager equation [23] is given by

$$\mu = \frac{2\varepsilon+n_2^2}{2+n_2^2}\sqrt{\frac{9000kT}{4\pi N\varepsilon}\left\{\frac{\varepsilon-n_1^2}{(2\varepsilon+n_1^2)\cdot c} + \left(\frac{\varepsilon-n_2^2}{2\varepsilon+n_2^2} - \frac{\varepsilon-n_1^2}{2\varepsilon+n_1^2}\right)\cdot\frac{M_2}{1000\cdot d_2}\right\}} \qquad (2)$$

Based on this equation, three different methods (which, in the following, are denoted as Method B, C, D) were employed to evaluate dipole moments from the dielectric measurements.

Method B1: evaluation of dipole moments μ for each concentration according to eq. (2) and extrapolation to infinite dilution.

Method B2: rigorous statistical evaluation of a concentration series according to the least square sum condition

$$\sum\left(\varepsilon_{calc}-\varepsilon_{exp}\right)^2=\min. \qquad (3)$$

Eq. (2) is readily transformed into

$$\left(1-\theta_2\right)\cdot\frac{\varepsilon-n_1^{\,2}}{2\varepsilon+n_1^{\,2}}+\theta_2\cdot\frac{\varepsilon-n_2^{\,2}}{2\varepsilon+n_2^{\,2}}=\frac{4\pi N\mu^2}{9000\cdot kT}\cdot\left(\frac{2+n_2^{\,2}}{2\varepsilon+n_2^{\,2}}\right)^2\cdot\varepsilon\cdot c \qquad (4)$$

where θ_2 denotes the volume fraction of the solute

$$\theta_2=\frac{M_2\cdot c}{1000\cdot d_2} \qquad (5)$$

This equation can be treated by successive approximations. For a trial value of μ the equation is solved numerically for ε; this is repeated with all available values for c and with the same value of μ, and then, the sum of squares, $\Sigma(\varepsilon_{calc}-\varepsilon_{exp})^2$, is calculated. The whole procedure is repeated with different values of μ to find the value of μ yielding the minimum sum of squares.

Method B3: involves a most convenient graphical evaluation in which the following two auxiliary variables x and y were plotted against each other:

$$x=\left(\frac{2+n_2^{\,2}}{2\varepsilon+n_2^{\,2}}\right)^2\cdot\varepsilon\cdot c \qquad (6a)$$

$$y=\left(1-\theta_2\right)\cdot\frac{\varepsilon-n_1^{\,2}}{2\varepsilon+n_1^{\,2}}+\theta_2\cdot\frac{\varepsilon-n_2^{\,2}}{2\varepsilon+n_2^{\,2}} \qquad (6b)$$

According to eq. (4) these variables are proportional to each other. The dipole moment is readily calculated from the slope of a linear regression line through the origin according to the following equation

$$\mu=\sqrt{\frac{9000\cdot kT}{4\pi N}\cdot S}=0.5051\cdot\sqrt{S\cdot T} \qquad (7)$$

where the slope, S, is calculated by

$$S=\frac{\sum_i y_i\cdot x_i}{\sum_i x_i^{\,2}} \qquad (8)$$

the index i denoting different measurements.

Comparison of Different Evaluation Methods

The differences between dipole moments evaluated by methods A, and B1-B3 are very small in practice. Assignment of configurations and even further consequences are independent on which method of evaluation has been used. The excellent agreement of dipole moments calculated by method B2 and B3 is remarkable. The linearized form of the Onsager equation (method B3) is a convenient way to calculate dipole moments. From a statistical point of view method B3 is inferior to method B2 because the experimental value, ε, enters both x and y in eq. (6). Although in certain cases linearized equations may lead to erroneous results [24], in our particular case, the inaccuracy inherent in the transformation, eq. (6), is negligible.

Table 2. Dipole moments evaluated according to methods A, B1 - B3; 1 Debye (1D) = 3.334·10^{-30} Cm.

model compound	cpd. no.	solvent	dipole moment (D) according to method			
			A	**B1**	**B2**	**B3**
$(H_3C)_3C$-CH_2Cl	**2**	C_6H_{12}	2.05	2.08	2.02	2.01
	2	C_6H_6	1.92	2.01	1.98	1.96
H_2C=$C(C_2H_5)Cl$	**3**	C_6H_{12}	1.79	1.80	1.75	1.73
	3	C_6H_6	1.59	1.64	1.60	1.58
H_2C=$C(C(CH_3)_3)Cl$	**4**	C_6H_{12}	1.78	1.81	1.77	1.75
	4	C_6H_6	1.55	1.62	1.60	1.59
H_5C_2-CH=CHCl	***Z*-5**	C_6H_{12}	1.65	1.66	1.62	1.60
	***Z*-5**	C_6H_6	1.56	1.64	1.60	1.58
H_5C_2-CH=CHCl	***E*-5**	C_6H_{12}	1.87	1.87	1.82	1.80
	***E*-5**	C_6H_6	1.79	1.85	1.79	1.78
$(H_3C)_3C$-CH=CHCl	***Z*-6**	C_6H_{12}	1.42	1.42	1.40	1.39
	***Z*-6**	C_6H_6	1.42	1.49	1.47	1.46
$(H_3C)_3C$-CH=CHCl	***E*-6**	C_6H_{12}	1.81	1.81	1.77	1.76
	***E*-6**	C_6H_6	1.86	1.93	1.88	1.87
$(H_3C)_3C$-CH=$C(C(CH_3)_3)Cl$	***Z*-7**	C_6H_{12}	2.05	2.06	2.02	2.00
	***Z*-7**	C_6H_6	1.50	1.58	1.57	1.56
$(H_3C)_3C$-CH=$C(C(CH_3)_3)Cl$	***E*-7**	C_6H_{12}	2.41	2.40	2.33	2.31
	***E*-7**	C_6H_6	2.18	2.24	2.20	2.18
$(H_3C)_3C$-CH=C=C=$C(C(CH_3)_3)Cl$	***Z*-8**	C_6H_{12}	1.82	1.81	1.73	1.72
	***Z*-8**	C_6H_6	1.57	1.61	1.58	1.57
$(H_3C)_3C$-CH=C=C=$C(C(CH_3)_3)Cl$	***E*-8**	C_6H_{12}	2.50	2.47	2.35	2.33
	***E*-8**	C_6H_6	2.00	2.04	1.95	1.94

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