

An NMR and Quantum Mechanical Investigation of Solvent Effects on Conformational Equilibria of Butanedinitrile

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Received April 12, 2002

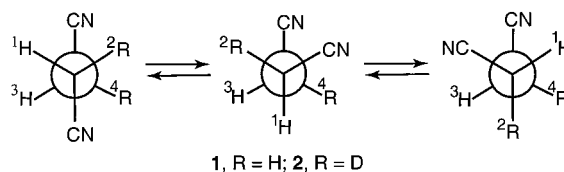
Abstract: Vicinal proton–proton NMR couplings and ab initio quantum mechanics have been used to investigate solvent effects on conformational equilibria of butanedinitrile. The trans and gauche conformations are about equally favored at room temperature in solvents of low dielectric constant while the equilibrium is essentially the statistical proportions of one-third trans and two-thirds gauche in water with a high dielectric constant. The coupling assignments were confirmed with the aid of stereospecific deuterium-labeled (*R,R* or *S,S*)-1,2-dideuteriobutanedinitrile. The calculations support the observed trends. Similar results were observed for 1,2-dibromo- and dichloroethanes.

Introduction

Among the several influences that are believed to be important in determining the positions of conformational equilibria of simple 1,2-disubstituted ethanes in solution is the gauche effect.^{1,2} One of the classic cases is that of 2-fluoroethanol, which shows a preference for its gauche over trans conformations on the order of 2.7 kcal/mol.³ The notion that this preference is the result of hydrogen bonding between the substituents is at variance with (1) the fact that similar preferences are exhibited by both 2-fluoroethyl acetate and 2-fluoroethyl trichloroacetate⁴ and (2) that, on dilution in tetrachloromethane solution, the hydroxyl proton of 2-fluoroethanol shows the typical upfield shift behavior of intermolecularly hydrogen-bonded alcohols,³ such as ethanol.^{5,6} Other cases where gauche predominates, 2-fluoroethylamine, 2-chloroethylamine, and their corresponding ammonium salts in water, have been provided by Abraham.⁷ These workers⁸ subsequently made a thorough study of *trans*-2-fluorocyclohexanol and concluded that F–OH–O hydrogen bonding is an important contributor to the observed preference for the gauche–gauche conformation. Be this as it may; there is clearly still something that appears to be a gauche effect as witnessed by

the cases cited above and the failure of 2-fluoroethanol to appear to be intramolecularly hydrogen bonded in dilute tetrachloromethane. A recent and comprehensive study⁹ has been made of the changes with solvent polarity of conformational equilibria of several 1-chloroethanes carrying as the 2-substituent: chlorine, fluorine, and cyano groups. The results indicate that the gauche effect is very much a function of solvent and, with the compounds studied, is actually a rather strong “trans effect” in the gas phase and in nonpolar solvents. The results to be reported below are somewhat different in that the solvent effects are very much smaller, but in general, the trends are much the same.

If we consider the gauche effect as it is exhibited in the gas phase or in nonpolar solvents, the simple perception could well be that the gauche effect is associated with strongly electron-attracting groups, because strong gauche preferences are displayed by 1,2-dihaloethanes and the other compounds cited above.^{2,9} However, the situation is clearly more complicated as seen from several theoretical studies, but it appears that some of the qualitative arguments (van der Waal’s radii and V_2 potential) advanced to explain the gauche preference of 1,2-difluoroethane² suggest that the gauche effect might also be quite important for butanedinitrile **1**. Indeed, **1** seems particularly



suitable as a test for the importance of electronegativity, because it is unlikely to have large steric effects, intramolecular van

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der Waals attractive effects, or intramolecular hydrogen bonding. But it does have highly polar, electron-attracting substituents. However, in regard to the substituents, we need a measure of electronegativity that can be reasonably applicable to the compounds in question. Thus, is the electron-attracting influence of two vicinal cyano groups attached to ethane to be taken as the equivalent of the electron-attracting effects corresponding to fluorine, hydroxyl, or amino groups? A reasonable comparison would be to use the sums of the appropriate Taft σ^+ values, which measure the electron-attracting effects of substituents in aliphatic systems.^{10,11} These sums for fluoroethanol are $3.2(\text{F}) + 1.55(\text{OH}) = 4.75$ and $2 \times 3.6(\text{CN}) = 7.2$, so that the pair of cyano groups should surely be expected to have the larger overall electronegative influence. We have calculated conformational equilibria for **1** in the gas phase, as well as in benzene and water solutions, and have measured the vicinal proton–proton coupling constants in several different solvents that provide equilibrium proportions of gauche and trans for comparison. A check on the gas-phase calculations is provided by the dipole moment data of Smythe.¹²

Experimental Section

Sample Preparation. The butanedinitrile and propionitrile samples were commercial materials purchased from Chem Service and Lancaster, respectively. The 1,2-(*R,R* or *S,S*)-dideuteriobutanedinitrile **2** was synthesized from fumaronitrile purchased from Aldrich. To synthesize this compound, 1.0 g of fumaronitrile and 0.01 g of Wilkinson's catalyst, $\text{RhCl}(\text{Ph}_3\text{P})_3$, were dissolved in 18 mL of dichloromethane and shaken in a Parr shaker at room temperature for 14 h with 40 psig of deuterium; the dichloromethane was then removed with a Rotovap. Some of the butanedinitrile samples for which couplings were measured were ^{13}C -labeled materials prepared in other research and to be described later. These did not give significantly different results.

NMR Spectra. Most of the NMR spectra were taken with a GE QE-300 NMR spectrometer. A 0.1 M solution of each sample was prepared in 100% atom % D D_2O (Aldrich) and in 100% atom % D toluene- d_8 (Aldrich), CDCl_3 (CIL), CD_2Cl_2 (CIL), and $\text{DMSO}-d_6$ (Aldrich). Solvents of especially low protium content were used as needed to facilitate observation of the ^{13}C satellites of **1**.

The ^1H NMR peaks were referenced to *p*-dioxane for D_2O or TMS for the other solvents. Typical conditions for observation of the ^{13}C satellites of **1** used 96 transients accumulated into 132K data points with a pulse delay of 9.33 s. Satisfactory spectra of propionitrile were obtained with 16 transients accumulated into 32K data points with a pulse delay of 9.33 s.

Spectra of 1,2-(*R,R* or *S,S*)-dideuteriobutanedinitrile **2** were taken at 22 °C with a 400-MHz Varian NOVA spectrometer. The deuterium was decoupled to allow the detection of the ^{13}C satellites on the proton lines of the remaining hydrogens. The importance of the deuterium decoupling is vividly illustrated by Figure 1, where the vicinal H–H couplings in the ^{13}C satellites of **2** in toluene- d_8 are wholly obscured by the geminal H–D couplings. In contrast, Figure 2 with deuterium decoupling shows the vicinal couplings clearly without ambiguity.

Coupling Constants. The $^3J_{\text{HH}}$ coupling constants for both butanedinitrile and propionitrile spectra were extracted from the observed line positions with the aid of a much-revised Macintosh version of the LAOCN3 program by BothnerBy and Castellano.¹³

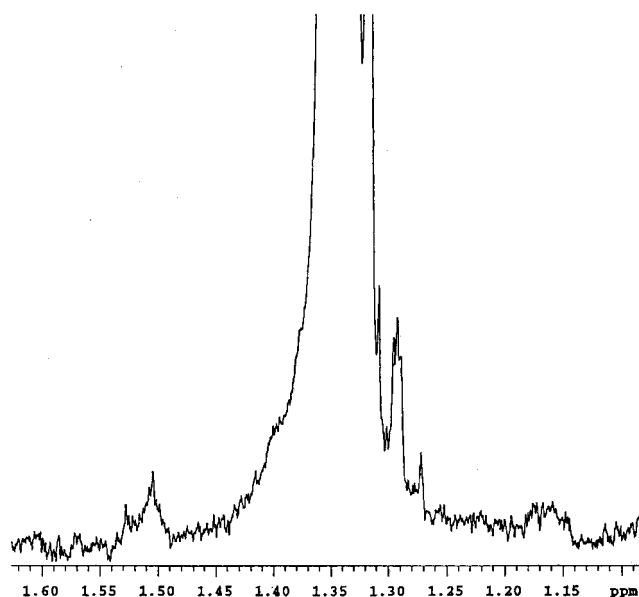


Figure 1. Proton spectrum showing the ^{13}C –H satellites of 1,2-(*R,R* or *S,S*)-dideuteriobutanedinitrile **2**, taken at 22 °C with a 400-MHz Varian NOVA spectrometer, not using deuterium decoupling.

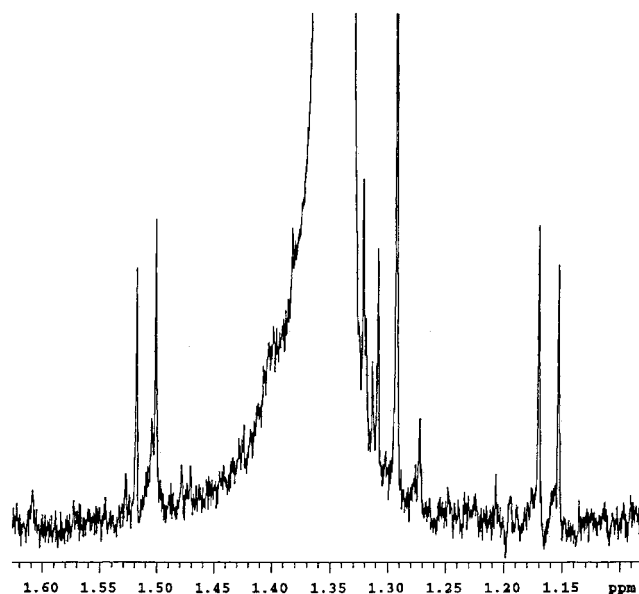


Figure 2. The same as Figure 1, except that now the deuterium was decoupled to allow detection of the vicinal H–H couplings

Theoretical Calculations. All quantum-mechanical calculations used the commercially available program Jaguar (PSGVB) version 2.35 (Schrodinger, Inc.) and involved Hartree–Fock geometry optimization followed by either a Hartree–Fock or LMP2^{14–16} energy and dipole moment calculation. LMP2 is a second-order Moller–Plesset perturbation¹⁴ calculation using localized orbitals. The calculations used no symmetry for both the Hartree–Fock and LMP2 calculations. The Pipek–Mezey^{17–24} localizations were employed for the LMP2 calculations.

Gas-phase calculations were made with the 6-31G**^{25–27} and the cc-pVTZ(-f) basis sets. The net dipole moment values calculated using

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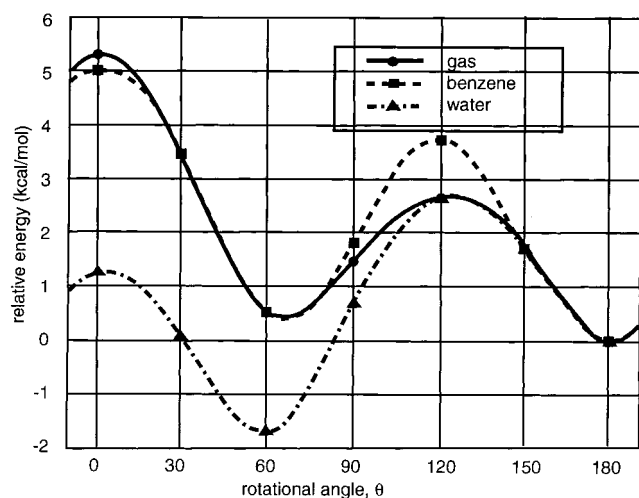


Figure 3. Calculated relative energies of succinonitrile in the gas, benzene, and water as a function of the C–C rotational angle obtained with a LMP2/cc-pVTZ(-f) energy calculation and HF/cc-pVTZ(-f) optimized geometry employing a continuum solvent model.

the 6-31G** basis set differ considerably from the experimental value of 3.4 D at 443 K.^{28–31} The cc-pVTZ(-f) basis set fared better because it is larger than 6-31G** and so is better able to describe the polarizations as well as the energies of butanedinitrile conformations. The results using cc-pVTZ(-f) basis set (see Figures 3 and 4) will be those discussed in what follows.

Calculations^{32–34} for solutions used the Poisson–Boltzmann Solver package, PS Solv, included in Jaguar with the default solvent parameters. The initial step was to calculate the gas-phase wave functions. The potential from those functions were then fitted to atomic charges.^{32–34} The solvent is represented as a layer of charges on the molecular surface by the Poisson–Boltzmann Solver. This layer of charges is then used in the next iteration of the quantum-mechanical calculations. The process is repeated until convergence is obtained.

To obtain a good description of the overall conformational energetics and dipole moment behavior of **1**, calculations of conformers were made with rotational angles θ between the substituents of 0°–180° in 30° steps. The results were interpolated with a cubic spline and the relative amounts of each rotamer calculated as a function of temperature by assuming a Boltzmann distribution:

$$A_{\theta_i} = \frac{e^{-\Delta E_{\theta_i}/kT}}{\sum_i e^{-\Delta E_{\theta_i}/kT}} \quad (1)$$

Here, A_{θ_i} is the relative amount of the conformer with the angle θ_i ,

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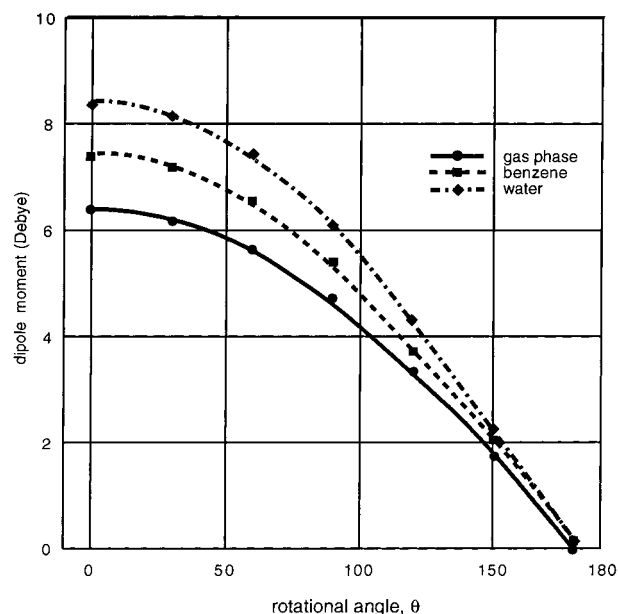


Figure 4. Dipole moment of succinonitrile calculated as a function of rotational angle in the gas, benzene, and water using LMP2/cc-pVTZ(-f) with HF/cc-pVTZ(-f) optimized geometry and a continuum solvent model.

Table 1. Measured Vicinal H–H Couplings and Calculated Percentages of Gauche for Butanedinitrile in Various Solvents

solvent	dielectric constant ^a	J_{13} , Hz	J_{14} , Hz	% gauche
toluene- <i>d</i> ₈	2.4	6.68 6.85 ^b	8.46	55.5 ± 1 56
CDCl ₃	4.8	7.55 7.31 ^b	7.00	70 ± 1 66
CD ₂ Cl ₂	9.08	7.31 ^c 7.20 ^d	6.91 ^c 7.20 ^d	69 ± 3 66
DMSO- <i>d</i> ₆	45	7.54	6.14	73.5 ± 5.5
D ₂ O	78	7.53	6.35	73 ± 4

^a The dielectric values are those of the protium solvents. ^b (*R,R* or *S,S*)-1,2-dideuteriobutanedinitrile. ^c Butanedinitrile-2,3-¹³C₂. ^d Butanedinitrile-1,4-¹³C₂.

ΔE_{θ_i} is the energy of the conformer θ_i , minus the energy of the trans conformation, k is the Boltzmann constant, and T is the temperature in kelvin.

With the relative population of each rotamer and its dipole moment, the net dipole moment as a function of temperature can be computed.

$$\mu^{\text{net}} = \sum_i A_{\theta_i} \mu_{\theta_i} \quad (2)$$

In this case, μ^{net} is the net dipole moment and μ_{θ_i} is the dipole moment of the rotamer with a particular value of θ . For both the A_{θ_i} and μ^{net} calculations, θ ranged from 0° to 180° in 1° increments.

In these calculations, we took gauche to be any conformer with a θ between 0° and 120° while trans was taken as any conformer with a θ between 120° and 180°. To obtain the relative amount of either gauche or trans rotamer, A_{θ_i} was summed over the angles that defined that rotamer.

Results and Discussion

Analysis by LAOCN3¹³ of the ¹³C satellites of **1** at 0.1 M concentration gave J_{13} and J_{14} values (averaged over the rotamer populations) that are listed for the various solvents in Table 1.

Because the J_{13} and J_{14} values are rather close to one another, it was not completely certain which experimental value should be assigned to which coupling. So the assignment for toluene-

d_8 was verified by examining the ^1H – ^1H J_{13} coupling of 1,2- (*R,R* or *S,S*)-dideuteriobutanedinitrile **2**, which yielded a couplings of 6.85 Hz in toluene- d_8 and 7.30 Hz in CDCl_3 .

The observed J_{13} and J_{14} coupling constants are related to the respective populations by

$$J_{\text{obsd}} = J_t T + J_g G \quad (3)$$

where J_{obsd} is either the observed J_{13} or J_{14} , J_t is the corresponding calculated J_{13} or J_{14} for the trans conformer, and J_g is the corresponding calculated J_{13} or J_{14} averaged over the two gauche conformers while T is the fraction of the trans, and G is the fraction of the gauche and $T + G = 1$. To calculate J_t and J_g , we have chosen to use the semiempirical method of Altona,³⁵ which is based on the Karplus curve. The empirical electronegativity of CN (λ) for this purpose was calculated to be 0.275 using the $^3J_{\text{HH}}$ coupling constant of 7.61 Hz for propionitrile obtained for D_2O and for toluene- d_8 . It was assumed that the other solvents would not be appreciably different. The value of 0.275 for in D_2O is consistent with Altona's reported value of 0.33, given the uncertainty of ± 0.1 Hz for the $^3J_{\text{HH}}$ coupling constant of propionitrile.

In this paper, we distinguish between the individual H–H dihedral angles (ϕ , which are related to specific spin–spin interactions) and the rotational angle (θ) between the substituent groups. In most conformational analyses, the ϕ values are assumed to have the perfectly staggered values of 60° and 180° for both the trans and gauche conformations. For the trans conformation of **1**, the individual ϕ angles of 60° and 180° seem reasonable, because the steric and other interactions between the substituents working to change the rotational angle θ should be minimal. However, for the gauche conformation, θ might arguably be greater, or less, than 60° because of steric or electrostatic interactions between the substituent groups. One way to test for deviations of gauche ϕ values from the perfectly staggered $\theta = 60^\circ$ is to compare conformational populations calculated from J_{13} and J_{14} with the aid of the Altona relation between ϕ and the gauche couplings with the assumption that the trans conformation is perfectly staggered. This we have done for the conformational populations of **1** with the J_g values associated with θ ranging from 55° to 65° . As θ increases, the calculated fraction of gauche increases on the order of 5% for D_2O and toluene- d_8 , but there is only a small improvement in the spread between the conformational populations calculated separately from J_{13} and J_{14} . The magnitude of the small improvement does not provide convincing evidence that θ is surely different from 60° and, furthermore, cannot by itself account for the fact that the gauche conformer is more favored in any of our measurements.

LMP2 calculations (see Figures 3 and 4) for the gas phase of **1** at 443 K predict 49.5% gauche and 50.5% trans. The corresponding calculated dipole moment of 2.95 D at 443 K is smaller than the experimental gas-phase value of 3.45 D at 443 K.²⁸ For benzene, 44.0% gauche and 56.0% trans is predicted at 298 K with a dipole moment of 3.20 D. The reported dipole moment of butanedinitrile in toluene at 30°C is 3.68 D.¹²

If the reported dipole moment of acetonitrile in toluene (3.40 D at 30°)¹² is used to represent the dipole–vector components

of the cyano groups in **1**, then the expected dipole moment in the gauche conformation with tetrahedral angles should be $2\mu_{\text{A}} \cos(109.5^\circ - 90^\circ) \cos(\theta/2)$, where θ is the rotational angle and $\mu_{\text{A}} = 3.40$ D. If θ is 60° , then the expected gauche moment turns out to be 5.512 D, which with the experimental moment of 3.68 D corresponds to 66.3% gauche, a larger figure than calculated from the NMR couplings. We put greater weight on the NMR measurements for two reasons. First, the temperature variation of the reported acetonitrile moment in toluene (0.27 D over 120°C)¹² seems unexpectedly large, 42% of that for butanedinitrile, which should be sensitive to conformational equilibrium shifts with temperature. Second, the measured polarization of the **1** may not be just the sum of the simple molecular dipole reorientation plus the electronic and atomic polarizations, but could also include what might be called “conformational polarization” in which the gauche and trans isomers decrease their conformational angles in response to the applied field. Such a conformational polarization does not have to be very large to account for the observed differences. Thus, if we assume that 5.512 D is the expected moment for the gauche form of the dinitrile and it amounts to 55.1% of the conformational total as deduced from the coupling constants for toluene, the predicted dipole moment without account of conformational polarization would be 3.03 D, which is within 6% of the 3.20 D calculated with LMP2 for benzene and unlikely to be much different from that for toluene. A conformational polarization contribution of 0.65 D does not seem unreasonable in comparison of the usual atomic polarization corrections of 0.2–0.3 D.

In any case, the results with the Poisson–Boltzmann solvation module within PSGVB (Figure 4) do suggest that simple quantum-chemical continuum solvation models can be useful for predicting conformational equilibria at least with nonpolar solvents.³⁶

The dipole moment of **1** has not been reported for water and so cannot be compared with the results from the theoretical calculations or the coupling data, the latter of which indicate about 72.7% gauche in contrast to 56% for toluene- d_8 . The theoretical calculations also suggest more gauche, but over-exaggerate it, leading to expectation at 298 K of 96.7% gauche and 3.3% trans, which would correspond to $J_{13} = 9.11$ Hz and $J_{14} = 4.10$ Hz.

The predicted strong preference for gauche in water follows the calculated solvation energy as a function of dihedral angle for **1** in water (see Figure 5), suggesting that **1** will be best solvated when $\theta = 0^\circ$. The same trend is also seen for benzene, but here the maximum change in solvation energy with θ is only tenths of a kilocalorie per mole compared ~ 1.3 kcal/mol for water. The calculated difference in the solvation energy as a function of θ accounts well for the difference in gauche conformation between toluene- d_8 and water.

The overall ab initio solvation energy calculation has three components²⁹ of which two are essentially insensitive to θ : the change in energy of the solute associated with the distortion of the wave function for the gas phase by the solvent dielectric and a cavitation term.²⁹ The third, most important term, which is sensitive to θ , is the total solvent energy and it includes changes in the polarization of the solvent by the solute.^{29,31}

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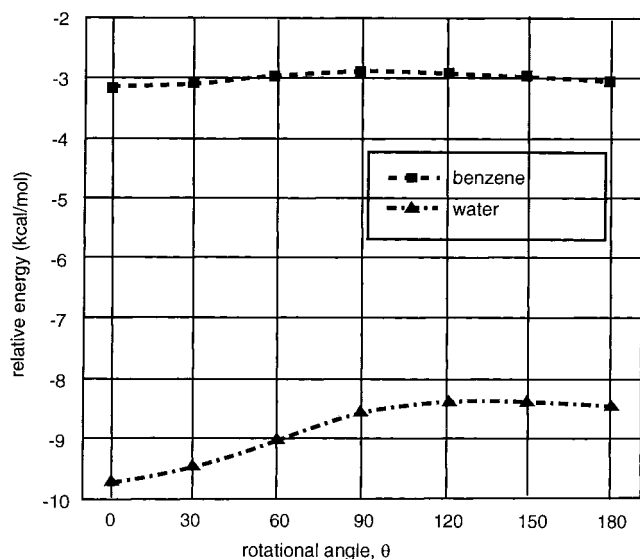


Figure 5. Calculated solvation energies for succinonitrile as a function of rotational angle in benzene and water calculated using LMP2/cc-pVTZ(-f) with HF/cc-pVTZ(-f) optimized geometry employing a continuum solvent model.

When the polar nitrile groups are trans to one another, they must be solvated individually. But when close to one another, they are likely to be better solvated as essentially a single entity with fewer solvent molecules being polarized. Because polarization of the solvent by the solute depends on the solvent dielectric constant, the effect should be smaller for benzene and toluene, which have dielectric constants of less than 2.4 at 25 °C compared to the nearly 80 for water.

Abraham^{8,37–40} used classical dielectric theory to investigate energy differences between the gauche and trans conformers in solution with account being taken of the dipole moment and polarizability of the solvent along with the dipole and quadrupole moments of the respective conformers. While the procedure is not applicable to **1** and the solvents used here, it does suggest that conformational equilibria studies are sensitive to solvent dielectric properties and not necessarily determined by subtle quantum influences. However, it is not wholly clear whether a high dielectric constant medium will tend to favor gauche for highly polar groups, while a small dielectric constant will favor trans. A substantial trend toward gauche with higher dielectric constant was observed by Wiberg and co-workers⁴¹ in a substantial infrared and quantum-mechanical study of the conformational equilibria of the 1,2-dichloro- and 1-chloro-2-fluoroethanes, which for dichloroethane is closely paralleled by the work of Tomasi.⁹ The preferences reported by both groups for trans is very high in the gas phase and declines to about 2 to 1 in acetonitrile with dielectric constant 36. To further test this relation between dielectric constant and conformational equilibria, we have made comparisons of the splittings of the ¹³C satellites on the proton spectra of 1,2-dibromo- and 1,2-dichloroethane in toluene-*d*₈ and in necessarily very dilute solutions in D₂O. While the proportions of gauche and trans as

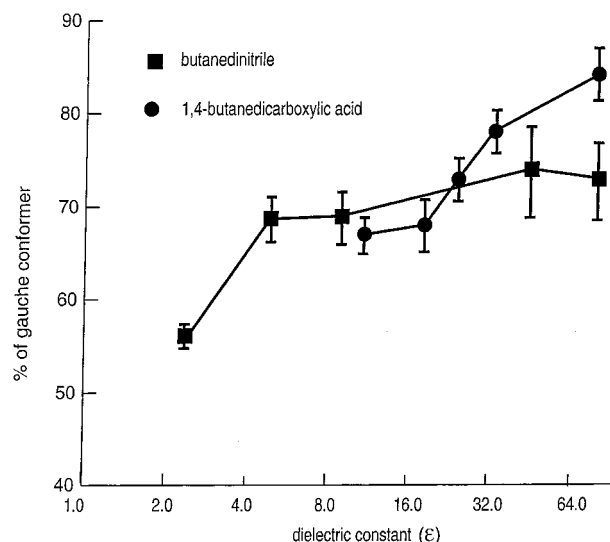


Figure 6. Observed coupling constants of butanedinitrile (see Table 1) and 1,4-butanedicarboxylic acid⁴² as a function of dielectric constant. The 1,4-butanedicarboxylic acid points used here are the ones in which the dihedral angle was assumed to be 60°. The curve would be of the same form, but shifted downward if a larger angle were assumed.

calculated separately from J_{13} and J_{14} show a somewhat larger spread than with **1**, the percentages of gauche were found to be on the order of 20–35% in toluene-*d*₈ and 60–80% in D₂O. In contrast, when our percentages of gauche from Table 1 are plotted against dielectric constant, the changes over the range are not large. Furthermore, when we include in Figure 6 the data obtained for 1,4-butanedicarboxylic acid in the solvent series of ROD with R = D, CD₃, C₂D₅, (CD₃)₂DC, and (CD₃)₃C, again the changes are rather small.⁴²

None of the results reported here support the idea that the gauche effect is necessarily associated with strongly electron-attracting substituent groups. Nor do they help explain the substantial gauche effects observed for 2-fluoroethanol and 1,2-difluoroethane for which there is very extensive literature and substantial controversy.⁴³

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We are also deeply indebted to the Summer Undergraduate Research Fellowship Program (SURF), the Beckman Institute of the California Institute of Technology, the E. I. Du Pont Co., and Dr. & Mrs. Chester M. McCloskey for their helpful financial assistance. D.R.K. is grateful for support of part of this research by a graduate fellowship from the Fannie and John Hertz Foundation. The quantum chemistry calculations reported here were funded by DOE-BCTR (DE-FG36-93CH105 81, David Boron). The facilities of the MSC are also supported by grants from NSF (CHE 95-22179 and ASC 92-100368), Chevron Petroleum Technology Co., Saudi Aramco, Asahi Chemical, Owens-Corning, Exxon, Chevron Chemical Co., Chevron Research and Technology Co., Avery-Dennison, Hercules, BP Chemical, and the Beckman Institute.

JA020535N

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