

doublet for the hydrogens of the methyl group.

In monomethylnaphthazarin the energy of one tautomer is 0.9 kcal/mol above that of the other. This difference destroys the symmetry of the potential surface. Our calculation shows that tunneling will not occur in this system for which the energy barrier is 28.1 kcal/mol for the concerted transfer and 25.0 kcal/mol for the stepwise transfers. If the hydrogen-bonded protons are initially placed in the positions they occupy in 2-methylnaphthazarin, they will remain there, without leaking through the barrier to the well representing 7-methylnaphthazarin. This would explain the  $^1\text{H}$

NMR spectrum of monomethylnaphthazarin, in which the 2-methyl tautomer seems to be the predominant structure, with two signals for the ring hydrogens, and in which both the quartet of the quinonoid ring and the doublet of the methyl group hydrogens are well defined.

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## Surface Tension of Ternary Polymeric Solution

J. D. Pandey\* and N. Pant

Contribution from the Department of Chemistry, University of Allahabad, Allahabad-211 002, India. Received June 18, 1981

**Abstract:** Assuming a ternary mixture to be made up of three binary mixtures, Flory's statistical theory has been extended to obtain a relationship for the surface tension of a ternary liquid mixture. In the light of above extension, the surface tension of a ternary mixture of hexane-decane-hexadecane polymer homologues has been predicted at 303.16 K, over a wide range of composition. There is reasonable agreement between theory and experiment.

### Introduction

Patterson et al.<sup>1-3</sup> have drawn attention to the close connection between the Flory theory of mixtures<sup>4,5</sup> and the corresponding states theory<sup>6</sup> of Prigogine by employing a simple cell model of the liquid state. Flory's statistical theory has been used, successfully,<sup>7-10</sup> to evaluate the surface tension of pure liquid and binary liquid mixtures through the use of suitable characteristic parameters (i.e., reduction parameters),  $p^*$ ,  $v^*$ , and  $T^*$ , for pressure, volume, and temperature, respectively. Recently Pandey<sup>11</sup> and Mishra<sup>12</sup> have also have shown the applicability of Flory's theory to predict sound velocity and surface tension at elevated pressure. It appears from the literature that no adequate theory is available for predicting the surface tension values in ternary liquid mixtures. In this connection the extension of the relationships for the surface tension of binary mixtures to the case of ternary systems is of interest. In the present paper Flory's statistical theory has been extended to evaluate the characteristic parameters of ternary liquid mixture, which in turn have been employed to predict the surface tension of hexane-decane-hexadecane polymer homologues at 303.16 K.

### Theoretical Section

Patterson and Rastogi<sup>7</sup> in their extension of the corresponding states theory dealt with the surface tension by using as the reduction parameter

$$\sigma^* = k^{1/3} p^{*2/3} T^{*1/3} \quad (1)$$

called the characteristic surface tension of the liquid. Here  $k$  is the Boltzmann constant. Starting from the work of Prigogine and Saraga,<sup>13</sup> they derived a reduced surface tension equation which in the case of a van der Waals liquid can be written as

(1) Patterson, D.; Bhattacharya, S. N.; Picker, P. *Trans. Faraday Soc.* **1968**, *64*, 648.

(2) Patterson, D.; Delmas, G. *Trans. Faraday Soc.* **1969**, *65*, 708.

(3) Patterson, D.; Delmas, G. *Disc. Faraday Soc.* **1970**, *49*, 98.

(4) Flory, P. J. *J. Am. Chem. Soc.* **1965**, *87*, 1833.

(5) Abe, A.; Flory, P. J. *J. Am. Chem. Soc.* **1965**, *87*, 1838.

(6) Prigogine, I. "The Molecular Theory of Solutions"; North-Holland Publishing: Amsterdam, Netherlands, 1967.

(7) Patterson, D.; Rastogi, A. K. *J. Phys. Chem.* **1970**, *74*, 1067.

(8) Lam, V. T.; Benson, G. C. *Can. J. Chem.* **1970**, *48*, 3773.

(9) Pandey, J. D. *J. Chem. Soc., Faraday Trans. 2* **1980**, *76*, 1215.

(10) Mishra, R. L.; Pandey, J. D. *Chem. Scr.* **1977**, *11*, 117.

(11) Pandey, J. D. *J. Chem. Soc., Faraday Trans. 1* **1979**, *75*, 2160.

(12) Mishra, R. L. *J. Chem. Phys.* **1980**, *73*, 5301.

(13) Prigogine, I.; Saraga, L. *J. Chim. Phys. Phys.-Chim. Biol.* **1952**, *49*, 399.

$$\bar{\sigma}(\bar{v}) = M\bar{v}^{5/3} - \frac{\bar{v}^{1/3} - 1}{\bar{v}^2} \ln \frac{\bar{v}^{1/3} - 0.5}{\bar{v}^{1/3} - 1} \quad (2)$$

where  $M$  is the fraction of nearest neighbors that a molecule loses on moving from the bulk of the liquid to the surface. Its most suitable value<sup>7</sup> is 0.29, which is used in our calculations. Thus surface tension of a liquid in terms of Flory theory can be described by the expression

$$\sigma = \sigma^* \bar{\sigma}(\bar{v}) \quad (3)$$

The characteristic and reduced parameters involved in the above equation of surface tension can be evaluated by the following procedure in the case of a ternary mixture.

The intermolecular energy  $E_0$  for the liquid is expressed by<sup>4</sup>

$$E_0 = Nrs\eta/2v \quad (4)$$

where  $N$  is the number of molecules,  $v$  is the volume per segment,  $rs$  is the number of contact sites, and  $\eta$  is a constant characterizing the energy of interaction for a pair of a neighboring sites.

The reduced equation of state derived from the resulting partition function is given by<sup>4</sup>

$$\frac{\bar{p}\bar{v}}{\bar{T}} = \frac{\bar{v}^{1/3}}{\bar{v}^{1/3} - 1} - \frac{1}{\bar{v}\bar{T}} \quad (5)$$

The reduced quantities  $\bar{p}$ ,  $\bar{v}$ , and  $\bar{T}$  are given by

$$\bar{p} = p/p^* = 2pv^{*2}/s\eta \quad (6)$$

$$\bar{T} = T/T^* = 2v^*ckT/s\eta \quad (7)$$

$$\bar{v} = v/v^* = V/V^* \quad (8)$$

Thus

$$p^* = ckT^*/v^* \quad (9)$$

where  $V = rv$  is the molar volume. The isobar at zero pressure is

$$T^* = \frac{T\bar{v}^{1/3}}{\bar{v}^{1/3} - 1} \quad (10)$$

From which

$$\bar{v}^{1/3} = \frac{\alpha T}{3(1 + \alpha T)} + 1 \quad (11)$$

Table I. Parameters of the Pure Component Liquids at 303.16 K

comp	$10^3\alpha$ , K <sup>-1</sup>	$\beta_{\Gamma}$ , T Pa <sup>-1</sup>	$\tilde{v}$	$V^*$ , cm <sup>3</sup> mol <sup>-1</sup>	$T^*$ , K	$p^*$ , J cm <sup>-3</sup>
hexane	1.416	1750	1.3313	99.530	4434	434.5
decane	1.055	1196	1.2623	156.005	5120	425.9
hexadecane	0.890	905	1.2278	240.612	5626	449.2

where  $\alpha$  is the thermal expansion coefficient at  $p = 0$  (or, without appreciable error, at 1 atm). The temperature derivative of eq 5 at constant volume evaluated for  $p = 0$  gives

$$p^* = \alpha T \tilde{v}^2 / \beta T = \gamma T \tilde{v}^2 \quad (12)$$

where  $\beta T$  and  $\gamma$  are the isothermal compressibility and the thermal pressure coefficient respectively. The quantities  $T^*$ ,  $p^*$ , and  $V^*$  can be computed from  $\alpha$ ,  $\gamma$ , and  $V$  as prescribed by eq 7-12.

Here it is assumed that a ternary mixture can be considered to be made up of three binary mixtures. The molecules of the three components are divided into equal segments so that  $v^*_1 = v^*_2 = v^*_3 = v^*$ . Assuming the additivity of the core volumes of the components and adopting the same procedure employed in the case of binary mixtures, it is possible to evaluate the characteristic parameters in the case of a ternary mixture, the components being indexed by subscripts 1, 2, and 3.

Let  $A_{11}$ ,  $A_{22}$ ,  $A_{33}$ ,  $A_{12}$ ,  $A_{23}$ , and  $A_{31}$  represents the number of contact pairs between the respective species and let  $\eta_{11}/v$ ,  $\eta_{22}/v$ , etc. be the energies associated with each. Then intermolecular energy in the case of ternary mixture can be written as

$$-E_0 = (A_{11}\eta_{11} + A_{22}\eta_{22} + A_{33}\eta_{33} + A_{12}\eta_{12} + A_{23}\eta_{23} + A_{31}\eta_{31})/v \quad (13)$$

In light of the above assumption and definitions set forth in eq 4, it is possible to write

$$A_{12} + A_{31} + 2A_{11} = s_1 r_1 N_1$$

$$A_{23} + A_{12} + 2A_{22} = s_2 r_2 N_2$$

$$A_{31} + A_{23} + 2A_{33} = s_3 r_3 N_3$$

from which the intermolecular energy may be written

$$E_0 = s_1 r_1 N_1 \eta_{11} + s_2 r_2 N_2 \eta_{22} + s_3 r_3 N_3 \eta_{33} - (\Delta\eta_1 A_{12} + \Delta\eta_2 A_{23} + \Delta\eta_3 A_{31})/2v \quad (14)$$

where

$$\begin{aligned} \Delta\eta_1 &= \eta_{11} + \eta_{22} - 2\eta_{12} \\ \Delta\eta_2 &= \eta_{22} + \eta_{33} - 2\eta_{23} \\ \Delta\eta_3 &= \eta_{33} + \eta_{11} - 2\eta_{31} \end{aligned} \quad (15)$$

It will be assumed that random mixing of three components is taking place. Furthermore, it is also assumed that a species of kind  $i$  neighbors any given site to be equal to its site fraction  $\theta_i$ , which is defined for ternary mixtures as follows:

$$\theta_3 = 1 - \theta_1 - \theta_2 = s_3 r_3 N_3 / s \bar{r} N \quad (16)$$

and

$$\theta_2 = 1 - \theta_1 - \theta_3 = s_2 r_2 N_2 / s \bar{r} N$$

On this basis

$$\begin{aligned} A_{12} &= s_1 r_1 N_1 \theta_2 = s_2 r_2 N_2 \theta_1 \\ A_{23} &= s_2 r_2 N_2 \theta_3 = s_3 r_3 N_3 \theta_2 \\ A_{31} &= s_3 r_3 N_3 \theta_1 = s_1 r_1 N_1 \theta_3 \end{aligned} \quad (17)$$

where

$$\bar{r} = (r_1 N_1 + r_2 N_2 + r_3 N_3) / N \quad (18)$$

$$s = (s_1 r_1 N_1 + s_2 r_2 N_2 + s_3 r_3 N_3) / \bar{r} N \quad (19)$$

$$N = N_1 + N_2 + N_3$$

By substituting eq 16 and 17 into eq 14 we have

$$\frac{-E_0}{\bar{r} N} = \frac{s}{2v} [\theta_1 \eta_{11} + \theta_2 \eta_{22} + \theta_3 \eta_{33} - \theta_1 \theta_2 \Delta\eta_1 - \theta_2 \theta_3 \Delta\eta_2 - \theta_3 \theta_1 \Delta\eta_3] \quad (20)$$

Defining the segment fractions  $\psi_3$ ,  $\psi_2$ , and  $\psi_1$  by

$$\psi_3 = 1 - \psi_1 - \psi_2 = r_3 N_3 / \bar{r} N \quad (21)$$

$$\psi_2 = 1 - \psi_1 - \psi_3 = r_2 N_2 / \bar{r} N$$

we have

$$1/\bar{r} = \psi_1/r_1 + \psi_2/r_2 + \psi_3/r_3 \quad (18')$$

$$s = \psi_1 s_1 + \psi_2 s_2 + \psi_3 s_3 \quad (19')$$

$$\theta_i = \psi_i s_i / s \quad (22)$$

The characteristic pressures for the pure components are given

Table II. Experimental and Predicted Values of Surface Tensions for the Mixtures of Hexane ( $x_1$ ), Decane ( $x_2$ ), and Hexadecane ( $x_3$ ), Polymer Homologues at 303.16 K

mole fract ( $x_2$ )	mole fract ( $x_3$ )	$\tilde{v}$	$T^*$ , K	$p^*$ , J cm <sup>-3</sup>	$\sigma^*$ , dyn cm <sup>-1</sup>	$10^5(\tilde{v})$	$\sigma_{\text{calcd.}}$ dyn cm <sup>-1</sup>	$\sigma_{\text{exptl.}}$ dyn cm <sup>-1</sup>	$\Delta$ , %
0.9491	0.0509	1.2597	5153	427.4	235.10	9758	22.94	23.16	0.9
0.8256	0.1744	1.2538	5231	430.8	237.53	9932	23.59	23.82	0.9
0.7346	0.2654	1.2500	5284	433.3	239.25	10052	24.05	24.18	0.5
0.5988	0.4012	1.2447	5359	436.7	241.62	10223	24.70	24.79	0.4
0.8580	0.0000	1.2689	5042	426.5	233.08	9476	22.09	22.28	0.8
0.7532	0.1048	1.2630	5116	429.6	235.34	9651	22.71	22.44	-1.2
0.6457	0.2123	1.2576	5185	432.6	237.51	9814	23.31	22.74	-2.5
0.5975	0.2605	1.2553	5216	433.9	238.44	9885	23.57	23.06	-2.2
0.4467	0.4113	1.2489	5304	437.7	241.18	10087	24.33	23.24	-4.7
0.7329	0.0000	1.2753	4969	427.2	232.20	9268	21.58	21.68	0.5
0.6353	0.0976	1.2692	5042	430.1	234.40	9468	22.19	21.84	-1.7
0.4795	0.2534	1.2606	5150	434.4	237.64	9723	23.10	21.99	-5.0
0.3902	0.3427	1.2563	5207	436.8	239.36	9854	23.59	22.16	-6.4
0.3253	0.4076	1.2535	5224	436.5	239.54	9942	23.81	22.24	-7.0
0.4969	0.0000	1.2894	4818	428.8	230.41	8905	20.52	20.44	-0.4
0.3784	0.1185	1.2803	4920	432.4	233.30	9152	21.35	20.38	-4.7
0.3058	0.1911	1.2753	4977	434.4	234.93	9292	21.83	20.33	-7.4
0.1547	0.3422	1.2662	5088	438.4	238.13	9556	22.75	20.25	-12.3
0.0980	0.3989	1.2632	5124	439.6	239.12	9645	23.06	20.27	-13.8
0.3998	0.0000	1.2960	4751	429.7	229.63	8733	20.05	19.98	-0.3
0.2761	0.1237	1.2856	4856	433.3	232.77	9008	20.97	19.80	-5.9
0.1895	0.2103	1.2793	4935	435.7	234.74	9180	21.55	19.66	-9.6
0.1190	0.2808	1.2746	4990	437.6	236.30	9312	22.00	19.52	-12.7
0.0698	0.3300	1.2715	5027	438.9	237.34	9401	22.31	19.35	-15.3

by eq 6 to be

$$p^*_1 = \frac{s_1\eta_{11}}{2v^{*2}} \quad p^*_2 = \frac{s_2\eta_{22}}{2v^{*2}} \quad p^*_3 = \frac{s_3\eta_{33}}{2v^{*2}} \quad (23)$$

By analogy, we define (assuming  $X_{ij} = X_{ji}$ )

$$X_{12} = \frac{s_1\Delta\eta_{12}}{2v^{*2}} \quad X_{23} = \frac{s_2\Delta\eta_{23}}{2v^{*2}} \quad X_{31} = \frac{s_3\Delta\eta_{31}}{2v^{*2}} \quad (24)$$

Substituting the values from eq 23 into eq 20, we have

$$\frac{-E_0}{\bar{r}N} = \frac{s}{2v} \left[ \theta_1 \frac{p^*_1 2v^{*2}}{s_1} + \theta_2 + \theta_2 \frac{p^*_2 2v^{*2}}{s_2} + \theta_3 \frac{p^*_3 2v^{*2}}{s_3} - \frac{\theta_1\theta_2 X_{12} 2v^{*2}}{s_1} - \frac{\theta_2\theta_3 X_{23} 2v^{*2}}{s_2} - \frac{\theta_3\theta_1 X_{31} 2v^{*2}}{s_3} \right]$$

which gives

$$\frac{-E_0}{\bar{r}N} = \frac{s}{v} \left[ \frac{\theta_1}{s_1} p^*_1 + \frac{\theta_2}{s_2} p^*_2 + \frac{\theta_3}{s_3} p^*_3 - \frac{\theta_1\theta_2 X_{12}}{s_1} - \frac{\theta_2\theta_3 X_{23}}{s_2} - \frac{\theta_3\theta_1 X_{31}}{s_3} \right] v^{*2}$$

On simplification, one gets

$$-E_0/\bar{r}N = [\psi_1 p^*_1 + \psi_2 p^*_2 + \psi_3 p^*_3 - (\psi_1\theta_2 X_{12} + \psi_2\theta_3 X_{23} + \psi_3\theta_1 X_{31})] v^*/\bar{v} \quad (25)$$

By analogy with the energy for a pure component we define

$$-E_0/\bar{r}N = p^* v^*/\bar{v} = ckT^*/\bar{v} \quad (26)$$

For the ternary mixture, where

$$c = (c_1 r_1 N_1 + c_2 r_2 N_2 + c_3 r_3 N_3) / \bar{r}N$$

or

$$c = \psi_1 c_1 + \psi_2 c_2 + \psi_3 c_3 \quad (27)$$

Comparing eq 25 and eq 26, one obtains

$$p^* = [\psi_1 p^*_1 + \psi_2 p^*_2 + \psi_3 p^*_3 - (\psi_1\theta_2 X_{12} + \psi_2\theta_3 X_{23} + \psi_3\theta_1 X_{31})] \quad (28)$$

On the basis of eq 26–28, the characteristic temperature  $T^*$  for the ternary mixture is given by

$$T^* = p^* \left( \frac{\psi_1 p^*_1}{T^*_1} + \frac{\psi_2 p^*_2}{T^*_2} + \frac{\psi_3 p^*_3}{T^*_3} \right) \quad (29)$$

where the characteristic temperatures  $T^*_i$  are defined in accordance with eq 7.

Assuming the volume reduction parameter of the ternary mixture to be linear in mole fractions of the components, we have

$$V^* = x_1 V^*_1 + x_2 V^*_2 + x_3 V^*_3 \quad (30)$$

and

$$\bar{v} = V/(x_1 V^*_1 + x_2 V^*_2 + x_3 V^*_3) \quad (31)$$

where  $V$  is the molar volume of ternary mixture. From adoption of the familiar Berthelot relationship

$$\eta_{ij} = (\eta_{ii}\eta_{jj})^{1/2}$$

for homopolar species, the interaction parameters  $X_{12}$ ,  $X_{23}$ , and  $X_{31}$  can be readily computed from eq 24 and 15 as

$$\begin{aligned} X_{12} &= p^*_1 [1 - (p^*_2/p^*_1)^{1/2} (s_1/s_2)^{1/2}]^2 \\ X_{23} &= p^*_2 [1 - (p^*_3/p^*_2)^{1/2} (s_2/s_3)^{1/2}]^2 \\ X_{31} &= p^*_3 [1 - (p^*_1/p^*_3)^{1/2} (s_3/s_1)^{1/2}]^2 \end{aligned} \quad (32)$$

Thus, it is possible to calculate the surface tension of the ternary system by using eq 3 in the light of eq 28, 29, and 31.

## Results and Discussion

So that the calculations could be carried out, equation of state parameters for pure liquids have been taken from the literature.<sup>14,15</sup> The values of experimental surface tension due to Beglyarov et al.<sup>16</sup> has been used. Maximum bubble-pressure method, in an improved gas apparatus of the Pugachevich type,<sup>17</sup> has been used to determine the surface tension of a ternary polymeric solution. In the calculations, molar volume of the mixtures at different compositions have been calculated from the data of molar volumes of pure components.

The numerical evaluation of the characteristic parameters  $V^*$ ,  $T^*$ , and  $p^*$  for each of the pure components was carried out according to the procedure adopted by Flory. The interaction parameters have been calculated by using eq 32. In all calculations the interaction parameters  $X_{12}$ ,  $X_{23}$ , and  $X_{31}$  have been assigned the values 1.95, 4.56, and 10.24 J cm<sup>-3</sup>, respectively. Segments and site fractions of the ternary mixture, defined above, have been calculated by using eq 21 and 16, with the assumption that

$$s_i/s_j = (r_i/r_j)^{-1/3} = (V^*_i/V^*_j)^{-1/3}$$

for a spherical molecule.<sup>5</sup>

$$\Psi_3 = x_3/(x_3 + x_1 V^*_1/V^*_2 + x_2 V^*_2/V^*_3)$$

$$\Psi_2 = x_2/(x_2 + x_3 V^*_3/V^*_2 + x_1 V^*_1/V^*_2)$$

where  $\Psi_3 = 1 - \Psi_1 - \Psi_2$  and

$$\theta_3 = \Psi_3/[\Psi_3 + \Psi_1(V^*_3/V^*_1)^{1/3} + \Psi_2(V^*_3/V^*_2)^{1/3}]$$

$$\theta_2 = \Psi_2/[\Psi_2 + \Psi_3(V^*_2/V^*_3)^{1/3} + \Psi_1(V^*_2/V^*_1)^{1/3}]$$

where  $\theta_3 = 1 - \theta_1 - \theta_2$ .

Table I lists all the parameters for the pure components. The values of different reduced and characteristic parameters along with their experimental and predicted surface tension values have been recorded in Table II. A perusal of Table II reveals that the agreement between the calculated and experimental surface tension values is reasonable in spite of several assumptions and approximations involved in the theory. The range of deviation between calculated and experimental values is 0.4 to -15.3%. The range of  $\sigma$ 's observed is  $\pm 13\%$ . An elementary statistical analysis of the disparities between theory and experiment would be illuminating, e.g., if the three most discrepant results are ignored, the standard deviation of  $\Delta$  from its mean value is 3.2%. The mean value of  $\Delta$  for the 20 samples thus included is -2.75%.

The application of Prigogine corresponding state principle to this problem of evaluating the surface tension of a ternary liquid mixture has been carried out in the pragmatic spirit, as was that of the original derivation of Patterson and Rastogi.<sup>7</sup> We have applied eq 2 to the ternary mixture on the assumption that they are equivalent to single-component liquids. The corresponding state treatment of mixtures<sup>8</sup> described is somewhat unorthodox, since application of eq 2 to an equivalent single-component liquid effectively ignores differences in concentration occurring at the surface of the mixtures. Gibbs enrichment of a mixture surface by the component of lower surface tension is well known. The normal result is a lowering of mixture surface tension, which results in a negative deviation from a linear function of bulk mole fraction. That is why there is a tendency of our theoretical values to be higher than the experimental values. However, it would not be proper to say that this is the only reason for larger discrepancies. A part of the discrepancies may be attributed to the approximations made in the computation of the interaction parameters  $X_{ij}$ .

(14) Orwoll, R. A.; Flory, P. J. *J. Am. Chem. Soc.* **1967**, *89*, 6814.

(15) "CRC Handbook of Chemistry and Physics", 60th ed.; CRC Press: Boca Raton, FL, 1979–1980.

(16) Beglyarov, E. M.; Pugachevich, P. P.; Kamalyan, R. M. *Kolloidn. Zh.* **1974**, *36*, 14.

(17) Pugachevich, P. P.; Tokaev, A. G.; Kamalyan, R. M. *Arm. Khimich. Zh.* **1970**, *23*, 376.

The *n*-alkane molecules form random coils due to internal rotation about C-C bond, and this tendency increases with increase in chain length, hence the extent of coiling in hexadecane > decane > hexane. In the ternary *n*-alkane system, hexane, the component of lower surface tension, certainly is enriched in the surface, but even after the surface enrichment possibly the larger decane and hexadecane molecules are so oriented as to cover such a surface fraction that the mixture surface tension is linear vs. bulk mole fraction. The but enrichment by the component of lower surface tension (hexane) is greater in the higher concentration range of hexane, showing larger discrepancies in that region. The principle of corresponding states has been applied successfully to mixtures of *n*-alkanes,<sup>6,18,19</sup> which has been used as a basis in the

extension of Flory's statistical theory to enable calculation of surface tension.

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**Registry No.** Hexane, 110-54-3; decane, 124-18-5; hexadecane, 544-76-3.

(18) Prigogine, I.; Bellemans, A.; Naar-Collin, C. *J. Chem. Phys.* **1957** *26*, 751.

(19) Hijmans, J. *Physica* **1961**, *27*, 433.

## Interproton Coupling over Five Bonds ${}^5J(\text{H}-\text{C}_\alpha-\text{C}(\text{O})-\text{N}-\text{C}_\alpha-\text{H})$ in the Peptide Moiety: The Importance of Specific Association Effects

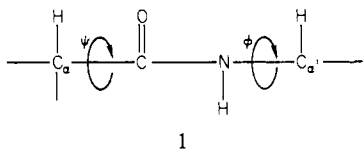
M. Barfield,\* F. A. Al-Obeidi, V. J. Hruby, and S. R. Walter

Contribution from the Department of Chemistry, University of Arizona, Tucson, Arizona 85721. Received August 14, 1981

**Abstract:** An experimental and theoretical study is presented of the conformational and solvent dependencies of long-range H-H coupling constants  ${}^5J(\text{H}-\text{C}_\alpha-\text{C}(\text{O})-\text{N}-\text{C}_\alpha-\text{H})$  in compounds which model the peptide backbone. Molecular orbital results for Fermi contact coupling in *cis*- and *trans*-*N*-methylacetamides do not follow a conformational dependence of the homoallylic type; negative values are predicted for most out-of-plane orientations of the  $\text{C}_\alpha-\text{H}$  bonds. In addition, the calculated values for  ${}^5J_{\text{HH}}^{\text{cis}}$  and  ${}^5J_{\text{HH}}^{\text{trans}}$  are of opposite signs in the planar conformation of *cyclo*-(Gly-Gly) and the boat conformation of *cyclo*-(Gly-Tyr). However, relative sign measurements show that these two coupling constants are of the same sign in *cyclo*-(Gly-Tyr), and that both are positive in *cyclo*-(Gly-Phgly). The inclusion of five water molecules in the MO calculations for *cis*-*N*-methylacetamide and ten water molecules in association with *cyclo*-(Gly-Gly) led to both positive  ${}^5J_{\text{HH}}^{\text{cis}}$  and  ${}^5J_{\text{HH}}^{\text{trans}}$ . As a consequence, any applicability of the empirical relationship of  ${}^5J(\text{H}-\text{C}_\alpha-\text{C}(\text{O})-\text{N}-\text{C}_\alpha-\text{H})$  to  $\phi$  and  $\psi$  angles in peptides does not have any theoretical basis in the molecular orbital theory for unhydrated amide bonds.

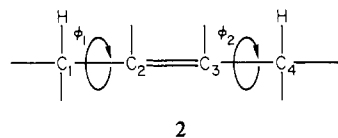
### Introduction

In studies of cyclic dipeptides it has been noted<sup>1,2</sup> that the syn coupling constants over five bonds  ${}^5J(\text{H}-\text{C}_\alpha-\text{C}(\text{O})-\text{N}-\text{C}_\alpha-\text{H})$  are smaller in magnitude than the anti values.<sup>3</sup> Subsequently, it was proposed<sup>4</sup> that this type of coupling could be diagnostic of syn and anti arrangements about the amide bond. The authors followed this by papers<sup>5</sup> which investigated the dependence of this type of coupling on the dihedral angles  $\phi$  and  $\psi$  in compounds which model the peptide backbone **1**. They assumed that the



1

conformational dependencies would be analogous to homoallylic coupling<sup>6</sup> such as would occur in the 2-butene moiety **2**. Hom-



2

oallylic coupling constants have been extensively investigated<sup>6-8</sup> and the  $\pi$ -electronic contributions are satisfactorily represented by the expression

$${}^5J_{\text{HH}}(\phi_1, \phi_2) = A \sin^2 \phi_1 \sin^2 \phi_2 + B \quad (1)$$

where the dihedral angles  $\phi_1$  and  $\phi_2$  are measured from the backbone plane as depicted in Figure 1. The calculated MO results<sup>7</sup> for  ${}^5J_{\text{HH}}(\phi_1, \phi_2)$  in *trans*-2-butene, which are plotted in Figure 2 as a function of these two dihedral angles, are also consistent with an angular dependence of the form of eq 1 with  $A = 5.0$  Hz and  $B \sim 0$ . However, eq 1 does not account for the well-documented differences between syn and anti arrangements about the double bond in **2** or the amide bond in **1**.<sup>4</sup> These differences can be interpreted in terms of negative contributions from the  $\sigma$ -electron framework in the syn arrangements.<sup>7</sup> It is also interesting to note that replacement of  $\text{C}_2$  or  $\text{C}_3$  in **2** with

(1) Kopple, K. D.; Ohnishi, M. *J. Am. Chem. Soc.* **1969**, *91*, 962.

(2) For reviews of cyclic dipeptide see: (a) Hruby, V. J. In "Chemistry and Biochemistry of Amino Acids, Peptides, and Proteins"; Weinstein, B., Ed.; Marcel Dekker: New York, 1974; Vol. 3, p 1. (b) Anteunis, M. J. O. *Bull. Soc. Chim. Belg.* **1978**, *87*, 627. (c) Bovey, F. A. In "Peptides, Polypeptides, and Proteins"; Blout, E. R., Bovey, F. A., Goodman, M., Lotan, N., Eds.; Wiley: New York, 1974; p 248.

(3) In accord with previous literature for this type of coupling the terms syn and anti will be used to denote the situation in which the  $\text{C}_\alpha$  and  $\text{C}_\alpha'$  carbon atoms in **1** ( $\text{C}_1$  and  $\text{C}_4$  carbon atoms in **2**) are on the same or opposite sides of the amide (double) bond, respectively. In cyclic molecules *cis* and *trans* denote protons on the same and opposite sides of the ring, respectively.

(4) Davies, D. B.; Khaled, Md. A. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1651; *Tetrahedron Lett.* **1973**, 2829.

(5) Davies, D. B.; Khaled, Md. A. *J. Chem. Soc., Perkin Trans. 2* **1976**, 187, 1238; 1327.

(6) Karplus, M. *J. Chem. Phys.* **1960**, *33*, 1842; Pinhey, J. T., Sternhell, S. *Tetrahedron Lett.* **1963**, 275.

(7) Barfield, M.; Sternhell, S. *J. Am. Chem. Soc.* **1972**, *94*, 1905.

(8) Jackman, L. M. Sternhell, S., "Applications of NMR Spectroscopy in Organic Chemistry"; Pergamon Press: New York, 1969; Chapter 4-4.