

The Anisotropy of the Aliphatic C-C Bond

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Abstract

In the conformational analysis of organic molecules by electric birefringence and Rayleigh scattering techniques, the value assigned to the aliphatic C-C bond, γ^{C-C} , is of fundamental importance. This communication discusses the implications of recent changes in the experimental parameters used to derive γ^{C-C} .

Molecular polarizability measurements have proved to be very useful for the examination of the solution state conformations of molecular species.¹ A corner-stone of this technique, when applied to the conformational analysis of organic molecules, is the value assigned to the bond polarizability anisotropy γ^{C-C} ($= b_L^{C-C} - b_T^{C-C}$),* of the axially symmetric $C(sp^3)-C(sp^3)$ bond. Neither γ nor b_L and b_T for individual bonds can be rigorously extracted² from molecular polarizability tensors obtained from experimental data. For example, in the case of alkane molecules with tetrahedral bond angles, the determinable polarizability parameter^{3,4} is

$$\Gamma = \gamma^{C-C} - 2\gamma^{C-H}$$

Le Fèvre *et al.*⁵ after reviewing previous determinations of the anisotropic polarizability of the C-H bond and from other considerations, argued for the retention of the assumption^{6,7} that the C-H bond is isotropically polarizable. This assumption, together with the values for Γ ($= 0.7 \pm 0.3$) and Σb_i^{C-C} ($= b_L^{C-C} + 2b_T^{C-C} = 1.491$) derived in ref. ⁵, yielded $b_L^{C-C} = 0.97$, $b_T^{C-C} = b_V^{C-C} = 0.26$. Redeterminations of the Kerr constants of carbon tetrachloride⁸ and cyclohexane⁹ (parameters used by

* Bond polarizability semi-axes (b_L , b_T , b_V) are quoted throughout in 10^{-24} cm³ units.

¹ Le Fèvre, C. G., and Le Fèvre, R. J. W., in 'Physical Methods of Chemistry' (Ed. A. Weissberger and B. Rossiter) (John Wiley: New York 1972).

² Smith R. P., and Mortensen, E. M., *J. chem. Phys.*, 1960, **32**, 508.

³ Sack, R. A., *J. chem. Phys.*, 1956, **25**, 1087.

⁴ Smith, R. P., and Mortensen, E. M., *J. chem. Phys.*, 1960, **32**, 502.

⁵ Le Fèvre, R. J. W., Orr, B. J., and Ritchie, G. L. D., *J. chem. Soc. (B)*, 1966, 273.

⁶ Le Fèvre, C. G., and Le Fèvre, R. J. W., *Rev. pure appl. Chem.*, 1955, **5**, 201.

⁷ Le Fèvre, C. G. and Le Fèvre, R. J. W., *Chem. Ind.*, 1955, 1121.

⁸ Le Fèvre, R. J. W., and Solomons, S. C., *Aust. J. Chem.*, 1968, **21**, 1703.

⁹ Le Fèvre, R. J. W., and Pierens, R. K., *Aust. J. Chem.*, 1972, **25**, 413.

Le Fèvre *et al.*⁵) together with recently reported¹⁰⁻¹² divergent estimates of Γ (see Table 1) have raised the question of whether the bond polarizability semi-axes quoted above should be modified. Table 1 contains the recalculated Γ values from ref.⁵ for cyclohexane both as the pure liquid and as a solute in carbon tetrachloride.

Table 1. Estimates of Γ

Authors	Γ	Comments
From cyclohexane		
Le Fèvre <i>et al.</i> ^{5,9}	0.75	pure liquid, λ 589 nm
Le Fèvre <i>et al.</i> ^{5,8}	0.65	solute in CCl ₄ , λ 589 nm
Foulani and Clement ¹⁰	0.70	pure liquid, λ 546 nm
From n-alkanes		
Bothorel ¹¹	0.87	for pure liquids and in solution, λ 546 nm
Patterson and Flory ¹²	0.54 ^A	solute in CCl ₄ , λ 633 nm

^A Calculated for a model in which the angles deviate from the tetrahedral value.

From the absolute intensities of Raman scattering of methane and benzene, Yoshino and Bernstein¹³ determined γ^{C-H} to be ± 0.312 and 0 respectively. Unfortunately, the sign ambiguity is not resolved by the above technique. If the positive and zero experimental measurements of γ^{C-H} as well as the extremes of Γ in Table 1 are used, the range of possible values for γ^{C-C} emerges as 0.54–1.49. These data, in conjunction with $\Sigma b_i^{C-C} = 1.491$,⁵ yield polarizability semi-axes for the C–C bond of $b_L^{C-C} = 0.86$ –1.49 and $b_T^{C-C} = b_V^{C-C} = 0.32$ –0. Some workers have arbitrarily chosen to let γ^{C-H} be 0.21,^{12,14-16} However, the arguments given by Le Fèvre, Orr and Ritchie⁵ in favour of the assumption that the C–H bond is isotropically polarizable are still valid. Hence, if the assumption that $\gamma^{C-H} = 0$ is used along with the mean value of Γ (0.70 ± 0.17) obtained from Table 1, the parameters $b_L^{C-C} = 0.96$, $b_T^{C-C} = b_V^{C-C} = 0.26$ are obtained. Clearly, these values are in accord with the bond polarizability semi-axes ($b_L^{C-C} = 0.97$, $b_T^{C-C} = b_V^{C-C} = 0.26$) currently used by the Sydney group.

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¹⁰ Foulani, P and Clement, C., *Bull. Soc. chim. Fr.*, 1969, 3462.

¹¹ Bothorel, P., *J. Colloid Interfac. Sci.*, 1968, 27, 529.

¹² Patterson, G. D., and Flory, P. J., *J. chem. Soc. Faraday II*, 1972, 1098.

¹³ Yoshino, T., and Bernstein, H. J., *J. molec. Spectrosc.*, 1958, 2, 241.

¹⁴ Fourche, G., and Bothorel, P., *J. chim. Phys.*, 1969, 66, 54.

¹⁵ Denbigh, K. G., *Trans. Faraday Soc.*, 1940, 36, 936.

¹⁶ Bunn, C. W., and Daubenny, R. P., *Trans. Faraday Soc.*, 1954, 50, 1173.