An Additivity Scheme for Conformational Energies in Substituted Ethanes

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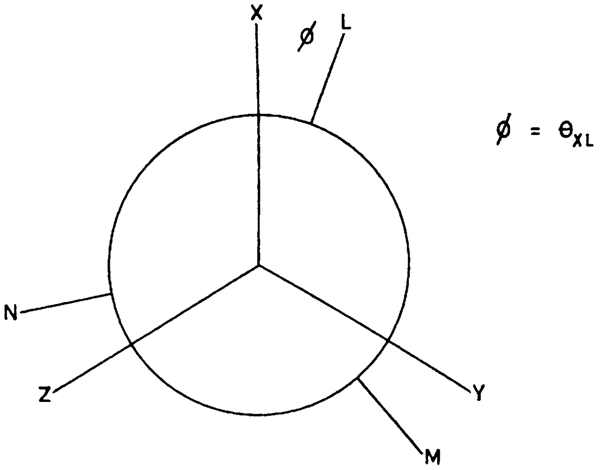
Summary *Ab initio* molecular orbital theory is used to demonstrate that conformational energies of polysubstituted ethanes may be well represented as linear combinations of conformational energies for ethane and appropriate mono- and 1,2-di-substituted derivatives.

IT is difficult to obtain detailed information about rotational potential functions for large molecules through direct application of standard techniques such as microwave spectroscopy and *ab initio* molecular orbital theory. For large molecules, the spectra are often complicated and the computations expensive. An attractive alternative proposition is to construct the potential functions from data on appropriate small molecules. Although additivity schemes have previously been proposed for this purpose,[1] insufficient data have hitherto been available to assess fully their reliability. In this communication, we use *ab initio* molecular orbital theory to test a method for obtaining conformational energies of polysubstituted ethanes from data on ethane and its mono- and 1,2-disubstituted derivatives.

TABLE 1. Calculated molecular potential constants (kcal mol^{-1})

	V_1	V_2	V_3
Ethane	—	—	$-2{\cdot}67$
Propane	—	—	$-2{\cdot}91$
Cyanoethane ..	—	—	$-2{\cdot}90$
n-Butane	$-4{\cdot}84$	$-2{\cdot}65$	$-3{\cdot}91$
1-Cyanopropane ..	$-1{\cdot}66$	$-1{\cdot}23$	$-3{\cdot}66$
1,2-Dicyanoethane	$-2{\cdot}05$	$-1{\cdot}03$	$-3{\cdot}50$

Our model is a refinement of an additivity scheme proposed by Wilson and co-workers.[1] We assume that in a substituted ethane XYZC-CLMN (I):



(I)

(i) interactions, $v^{XL}(\theta_{XL})$, between vicinal bonds (CX and CL at a dihedral angle θ_{XL}) may be expressed as truncated Fourier series[1]

$$v^{XL}(\theta_{XL}) = \sum_{n=1}^{3} \tfrac{1}{2} v_n^{XL}(1 - \cos n\theta_{XL}) \tag{1}$$

(ii) the total molecular potential $V(\phi)$ (where ϕ is a dihedral angle defining the molecular conformation) is the sum of the pairwise interactions $v^{IJ}(\theta_{IJ})$

$$V(\phi) = \sum_{I,J} v^{IJ}(\theta_{IJ}) \qquad (I = X,Y,Z;\ J = L,M,N) \tag{2}$$

(iii) $V(\phi)$ can itself be represented as a Fourier expansion:[2]

$$V(\phi) = \sum_{n=1}^{3} \tfrac{1}{2} V_n(1 - \cos n\phi) + \sum_{n=1}^{2} \tfrac{1}{2} V_n' \sin n\phi, \tag{3}$$

$$= \sum_{I,J} \sum_{n=1}^{3} \tfrac{1}{2} v_n^{IJ}(1 - \cos n\theta_{IJ}) \tag{4}$$

from (1) and (2).

The molecular potential constants V_n are related *via* (3) and (4) to the vicinal potential constants v_n^{IJ}. It follows[3] that the molecular potential constants for the general polysubstituted ethane XYZC–CLMN are related to the molecular potential constants for ethane and its mono- and di-substituted derivatives. For the particular case of the polysubstituted ethane, (±)-2,3-dicyanobutane (X=L=Me, Y = N = CN, Z = M = H in I), the relationship is expressed by equations (5).

$$V_1 = V_1^{\text{butane}} - \tfrac{1}{2} V_1^{\text{dicyanoethane}} - V_1^{\text{cyanopropane}} \tag{5a}$$

$$V_2 = V_2^{\text{butane}} - \tfrac{1}{2} V_2^{\text{dicyanoethane}} - V_2^{\text{cyanopropane}} \tag{5b}$$

$$V_3 = V_3^{\text{butane}} + V_3^{\text{dicyanoethane}} + 2V_3^{\text{cyanopropane}} + V_3^{\text{ethane}} - 2V_3^{\text{propane}} - 2V_3^{\text{cyanoethane}} \tag{5c}$$

$$V_1' = \sqrt{3}\,(\tfrac{1}{2} V_1^{\text{dicyanoethane}} - V_1^{\text{cyanopropane}}) \tag{5d}$$

$$V_2' = -\sqrt{3}\,(\tfrac{1}{2} V_2^{\text{dicyanoethane}} - V_2^{\text{cyanopropane}}) \tag{5e}$$

In order to test the validity of this approach, we have performed *ab initio* molecular orbital calculations[4] with the minimal STO-3G basis set[5] on ethane, propane, cyanoethane, butane, 1-cyanopropane, and 1,2-dicyanoethane, and on (±)-2,3-dicyanobutane itself. Calculations were carried out for all exactly eclipsed and staggered conformations, corresponding to 60° intervals in the dihedral angle ϕ. Bond angles formed by the substituents with the central C–C bond were assumed to be 112°. Bond angles unaffected by these constraints and all bond lengths were given standard values.†[6]

TABLE 2. Comparison of directly calculated and empirically estimated quantities for (±)-2,3-dicyanobutane[a]

	Direct calculation	Empirical estimate
	(V values in kcal mol^{-1})	
$V(0°)$	0	0
$V(60°)$	$-7{\cdot}13$	$-7{\cdot}06$
$V(120°)$	$-1{\cdot}54$	$-1{\cdot}28$
$V(180)$	$-8{\cdot}03$	-7.93
$V(240°)$	$-3{\cdot}29$	$-3{\cdot}30$
$V(300°)$	$-6{\cdot}92$	$-6{\cdot}94$
ϕ_A	62°	62°
ϕ_B	184°	184°
ϕ_C	294°	294°
V_A	$-7{\cdot}15$	$-7{\cdot}07$
V_B	$-8{\cdot}08$	$-7{\cdot}99$
V_C	$-7{\cdot}06$	$-7{\cdot}08$

[a] ϕ_A, ϕ_B, ϕ_C and V_A, V_B, V_C are the dihedral angles and potential energies, respectively, corresponding to the minima in the rotational potential function and were derived using (3).

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† Ideally, complete optimization of bond lengths and bond angles is desirable. However, such a refinement is at present computationally too expensive. The geometric parameter which is likely to show the largest variation with conformation is the angle formed by the substituent with the central C–C bond: L. Radom and J. A. Pople, *J. Amer. Chem. Soc.*, 1970, **92**, 4786. Our choice of 112° represents a compromise value for this angle.

Results for the simpler molecules are presented in Table 1 in terms of potential constants derived using (3) These potential constants lead *via* (5) and (3) to estimates of conformational energies for (±)-2,3-dicyanobutane which are compared with directly calculated values in Table 2.

The potential curve predicted from our additivity scheme agrees well with that obtained by direct calculation (Table 2). Our results suggest that this general approach may be useful for obtaining detailed information about potential functions describing internal rotation in large molecules.

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[1] See, for example, E. Saegebarth and E. B. Wilson, *J. Chem. Phys.*, **1967**, **46**, 3088; O. L. Stiefvater and E. B. Wilson, *J. Chem. Phys.*, **1969**, **50**, 5385; N. Sheppard, *Adv. Spectroscopy*, **1959**, **1**, 288.

[2] See, for example, L. Radom, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **1972**, **94**, 2371; L. Radom, W. A. Lathan, W. J. Hehre, and J. A. Pople, *ibid.*, **1973**, **95**, 693.

[3] Full details will be reported in a forthcoming paper: D. P. Craig, L. Radom, and P. J. Stiles, to be published.

[4] Calculations were carried out using the Gaussian 70 series of programmes: W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, program number 236, Q.C.P.E., University of Indiana, Bloomington, Indiana.

[5] W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **1969**, **51**, 2657.

[6] J. A. Pople and M. S. Gordon, *J. Amer. Chem. Soc.*, **1967**, **89**, 4253.

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