

## ON THE OPTICAL ACTIVITY OF PARAFFINIC HYDROCARBONS<sup>1</sup>

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**Abstract**—An expression for potential energy as a function of torsion angle about a saturated C–C bond is developed analytically. This equation is used in the development of two methods for the conformational analysis of paraffins—one based on consideration only of exactly staggered conformers and one giving consideration to energy at 1° intervals of torsion angle. Two methods of assigning molecular rotations to hydrocarbon conformers are considered. Various combinations of results so obtained are compared as ways to calculate rotations for paraffins.

The molecular rotation of a substance with flexible molecules is the sum of the rotations of the individual conformers ( $M_i$ ), each weighted to reflect the fractional contribution of the conformer to the molecular population ( $f_i$ ):

$$[M]_D = \sum M_i \cdot f_i \quad (1a)$$

We wish to consider here several methods for assigning values to each of the two parameters of this equation, using flexible paraffinic hydrocarbons as substrates for simplicity in both tasks.

### CONFORMATIONAL ANALYSIS

#### Conformational septs

It is at once evident that the “number” of conformers possible—and thus the number of items to be summed using Eq 1—depends on how large a difference in torsion angle is considered sufficient to make one conformer different from the next. For some purposes the level of discrimination may be high enough that a change of 1° in torsion angle is significant so that the number of conformers is 360°, where  $n$  is the number of conformationally significant bonds. In other cases torsion angle differences of 120° may suffice, reducing the number of conformers to 3°. We introduce here the concept of the “conformational sept” as a means of enjoying the convenience of dealing with small numbers of conformers while retaining the advantages of high discrimination. A conformational sept is a group of conformers differing from one another in torsion angles about selected bonds but related by the fact that they can be interconverted without crossing a torsional barrier. The probability of the occurrence of a particular sept is a function of the probability of occurrence of each of its members taken at some appropriately high level of discrimination, e.g., at torsion angle differences of 1°. A

property may be unsymmetrically distributed among the members of a sept so that the middle conformer is neither an extreme (in, e.g., potential energy) nor an average (in, e.g., rotatory power). A summing or averaging of the property over the whole sept in a suitable model system would take such skewing into account and provide a number which could be used with more complex systems just as though the sept actually contained only one member. Eq 1a, for example, becomes:

$$[M]_D = \sum \bar{M}_i \cdot \bar{f}_i \quad (1b)$$

where  $\bar{M}_i$  and  $\bar{f}_i$  are now sept properties. We will designate the septs about a saturated bond as  $P$ ,  $T$  and  $M$  as shown in Fig 1.

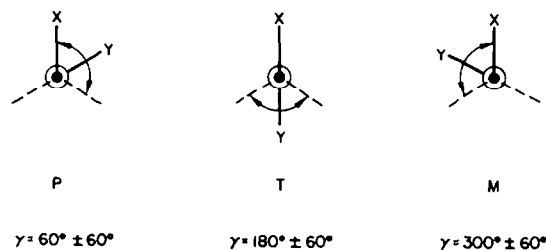


Fig 1. Conformational notation. The rear carbon atom, carrying group Y, rotates clockwise to give positive torsion angles.

#### Sept population factors

In our initial approach to this problem<sup>2</sup> we implicitly considered that the fraction of a substance present as a particular conformer could be defined in terms of *probability* or *population factors* ( $P^o$ ) for each significant bond. When this concept is made explicit it takes the form:

$$f_i = \frac{(P_A^0 \cdot P_B^0 \cdot P_C^0 \cdots P_N^0)_i}{\sum (P_A^0 \cdot P_B^0 \cdot P_C^0 \cdots P_N^0)} \quad (2a)$$

where  $P_{X_i}^0$  is a measure of the tendency of bond  $X$  to assume the particular conformation found in conformer  $i$ , standardized for energetic consistency in this and all other conformers. In our earlier work<sup>2</sup> substances were analyzed in terms of exactly staggered bond conformations which were either "allowed" ( $P^0 = 1$ ) or "forbidden" ( $P^0 = 0$ ), whence the product for each conformer had a value of either 1 or 0. If  $n$  conformers were allowed then the  $f$  value for each was  $1/n$  (as from Eq 2a or 2b). Each bond conformation was assigned a characteristic rotatory value ( $\Delta M_D$ ) and  $[M]_D$  was calculated as from (Eq 1a or 1b). We will refer to this as the original conformational dissymmetry model (method IA). We propose to retain these basic principles but, in this section, to consider more refined methods for ascertaining population factors ( $P$ ) and, thus, for assigning values for  $f$ .

The value of  $P_{X_i}^0$  is controlled by the potential energy of the bond conformation:

$$P_{X_i}^0 = \frac{N}{N_0} = e^{-E_{X_i}^0/RT} \quad (3a)$$

where  $N$  is the number of molecules having torsional energy  $E_{X_i}^0$ , relative to  $N_0$ , the number that would be present were the torsional energy zero. The torsional energy of staggered ethane is taken as our standard point of zero energy. Positive values of  $E^0$  result from van der Waals repulsions and negative values from attractions. We calculate population factors for conformational septs ( $\bar{P}_\gamma^0$ ) by summing for  $P^0$  at  $1^\circ$  intervals:

$$\bar{P}_\gamma^0 = \sum_{\Delta=1}^{\gamma-60^\circ+\gamma+60^\circ} e^{-E^0/RT} \quad (3a)$$

whence the sept fraction becomes:

$$\bar{f}_i = \frac{(\bar{P}_A^0 \bar{P}_B^0 \bar{P}_C^0 \cdots \bar{P}_N^0)_i}{\sum (\bar{P}_A^0 \bar{P}_B^0 \bar{P}_C^0 \cdots \bar{P}_N^0)} \quad (2b)$$

This method of conformational analysis will be used in what we will term the *sept dissymmetry model* (method IC). We will also consider an intermediate method of conformational analysis, using the energies of the exactly staggered conformers ( $\gamma = 60^\circ, 180^\circ$  and  $300^\circ$  only) to calculate populations; this is the characteristic feature of what we

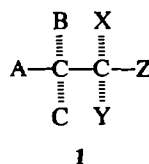
will term method IB, a refined conformational dissymmetry model.

### The conformational energy equation

We assume that the standard energy ( $E^0$ ) of a particular conformer of the simple substituted ethane 1 is adequately expressed as the sum of characteristic partial conformational energies ( $\delta E^0$ ) for pairwise interactions across the central bond, due account being taken of the torsion angle ( $\gamma$ ) between the members of each interacting pair:

$$E^0 = \sum \delta E_{(A-X)}^0 + \delta E_{(A-Y)}^0 + \dots \delta E_{(C-Z)}^0 \quad (4)$$

We assume further that it will be adequate for our purposes to obtain energies at  $60^\circ$  intervals since energy minima will occur at or near  $60^\circ, 180^\circ$  and  $300^\circ$  and maxima at or near  $0^\circ, 120^\circ$  and  $240^\circ$ , and to connect these points by means of an equation giving a smooth, continuous, sinusoidal line. It is obvious that such connections can be made in many ways, differing in the sharpness of the peaks and the breadth of the valleys; we have attempted to generate the connecting line with the simplest equation.



Analytically, a suitable equation requires one term of the form:  $A(1 + \cos 3\gamma)$  which gives maxima (2A) at  $\gamma = 0^\circ, 120^\circ$  and  $240^\circ$  and minima (0) at  $\gamma = 60^\circ, 180^\circ$  and  $300^\circ$ . This term appears in most discussions of the conformational properties of systems such as ethane. A second term, with both a plane of symmetry and a minimum at  $180^\circ$ —for example,  $B(1 + \cos \gamma)$  would allow the minima at  $60^\circ$  and  $300^\circ$  to be (equally) higher or lower than the one at  $180^\circ$ . Additional terms, each with a point of symmetry at  $180^\circ$  and values of zero at  $0^\circ, 180^\circ$  and  $360^\circ$  would allow for "fine tuning" of the intermediate minima and maxima.

One equation, of proper form, is based on the notion that the stresses of each eclipsed conformation decay with torsion angle as:  $X(1 + \cos \gamma)^n$ , as in Eq 5.

$$(E-E_{180}) = X(1 + \cos \gamma)^3 + Y[1 + \cos(\gamma - 120)]^3 + Z[1 + \cos(\gamma + 120)]^3 - \frac{7}{8}(Y + Z) \quad (5)$$

This reduces to one of the form discussed above:

$$(E-E_{180}) = A(1 + \cos 3\gamma) + B[1 + \cos \gamma - \frac{3}{2}(1 - \cos 2\gamma)] + C[\sin \gamma - \frac{3}{2} \sin 2\gamma]^* \quad (6)$$

\*This equation is a 3-parameter form of the 5-parameter equation:

$$V_{(\phi)} = \frac{1}{2}V_1(1 - \cos \phi) + \frac{1}{2}V_2(1 - \cos 2\phi) + \frac{1}{2}V_3(1 - \cos 3\phi) + V_1' \sin \phi + V_2' \sin 2\phi$$

We found this equation cumbersome to use in developing individual conformational energy values and have used, instead, Eq 7:

$$E^\circ = A(1 + \cos 3\gamma) + B(1 + \cos \gamma) + C \sin \gamma(1 + \cos \gamma) + D \sin \gamma(1 - \cos \gamma) + E_{180}^\circ \quad (7)$$

The third and fourth terms allow separate "fine tuning" of the intermediate minima and maxima: the third term has extremes at 60° and 300° and the fourth term at 120° and 240°. Taken together, they provide one term in  $\sin \gamma$ :  $(C + D)$  and one in  $\sin 2\gamma$ :  $(C - D)/2$ . In the early stages of this work it appeared that both of these terms were necessary; when, however, a fully interlocked set of conformational energies was obtained it was found that an equation of the form:

$$E^\circ = A(1 + \cos 3\gamma) + B(1 + \cos \gamma) + F \sin \gamma + E_{180}^\circ \quad (8)$$

would have been sufficient.

It is seen that if, for torsion about any particular bond, we can estimate energies for five of the minima and maxima we can, by a solution of simultaneous equations, obtain the parameters of Eq 7, whence values for  $E^\circ$  at any torsion angle can be obtained and, so, values for  $\bar{P}_i^\circ$  (Eq 3b) and  $\bar{I}_i$  (Eq 2b). The relationships among these parameters are shown in Table 1. The following key relationships make it a simple matter to obtain these parameters:

$$6A = E_0 + E_{120} + E_{240} - E_{60} - E_{180} - E_{300} \quad (9a)$$

$$3B = (E_{60} - E_{180}) + (E_{300} - E_{180}) \quad (9b)$$

$$3C + D = \frac{2}{\sqrt{3}}(E_{60} - E_{300}) \quad (9c)$$

$$C + 3D = \frac{2}{\sqrt{3}}(E_{120} - E_{240}) \quad (9d)$$

$$2A + 2B = E_0 - E_{180} = \frac{1}{2}(E_{60} + E_{300} - 2E_{180}) + \frac{1}{2}(E_{120} + E_{240} - 2E_{180}) \quad (9e)$$

### Conformational energies

We assume that a hydrogen atom in a *gauche* staggered ( $\gamma = 60^\circ$ ) relation to another hydrogen atom or to any alkyl group has a conformational energy of zero\*.

Values of 0.95 kcal/mol for the eclipsing interaction of two H atoms, (H, H)<sub>0</sub>, and 1.55 kcal/mol for the corresponding H-Me interaction, (H, CH<sub>3</sub>)<sub>0</sub>,

\*The assignment of conformational energies of other than zero to hydrogen-alkyl interactions leads to insuperable difficulties in assessing population probabilities of complex substances *via* multiplication of sept population factors ( $\bar{f}$ ). The difficulty arises because one cannot avoid including such interactions several times over.

Table 1. Relationships among the parameters of the conformational energy equations.

$\gamma$	$E^\circ - E_{180}^\circ$	
	Eq 7	Eq 8
0°	2A + 2B	2A + 2B
60°	$\frac{3}{2}B + \frac{\sqrt{3}}{4}(3C + D)$	$\frac{3}{2}B + \frac{\sqrt{3}}{2}F$
120°	$2A + \frac{1}{2}B + \frac{\sqrt{3}}{4}(C + 3D)$	$2A + \frac{1}{2}B + \frac{\sqrt{3}}{2}F$
180°	0	0
240°	$2A + \frac{1}{2}B - \frac{\sqrt{3}}{4}(C + 3D)$	$2A + \frac{1}{2}B - \frac{\sqrt{3}}{2}F$
300°	$\frac{3}{2}B - \frac{\sqrt{3}}{4}(3C + D)$	$\frac{3}{2}B - \frac{\sqrt{3}}{2}F$

give reasonably good fits to barriers for rotation that have been observed in ethane, propane, isobutane and neopentane (Table 2). Calculation of the van der Waals interaction for the eclipsed H-Me and H-t-Bu interactions by use of the equation of Hill<sup>3</sup> indicates that the latter interaction should be some 0.6 kcal/mol greater than the former, namely 2.15 kcal/mol. The most distant Me group of the t-Bu group is essentially without effect. A comparison of the interaction of a H atom (H) with an eclipsing Me (M), *gauche* Et and a t-Bu (B) group indicates that the energy of the second interaction should be the average of the first and third, 1.85 kcal/mol.

Table 2. Barriers to rotation in compounds containing methyl groups

Substance	$E_\sigma - E_{60}$ (kcal/mol)		
	Calculated	Observed	Reference
Ethane	2.85	2.9	a
Propane	3.45	3.3	b
Isobutane	4.05	3.9	b
Neopentane	4.65	4.8	b
		4.3	c

<sup>a</sup>D. R. Lide, Jr., *J. Chem. Phys.* **29**, 1426 (1958).

<sup>b</sup>J. G. Aston, in *Determination of Organic Structures by Physical Methods* (Edited by E. A. Braude and F. C. Nachod) Vol. 1, p. 525 Academic Press, New York, (1955)

<sup>c</sup>J. R. Durig S. M. Craven and J. Bragin, *J. Chem. Phys.* **52**, 2046 (1970)

An analysis of the energies of interactions among Me (M), *gauche* Et and t-Bu (B) groups as a function of dihedral angle is shown in Charts 1 ( $\gamma = 0^\circ$ ), 2 ( $\gamma = 60^\circ$ ), 3 ( $\gamma = 120^\circ$ ) and 4 ( $\gamma = 180^\circ$ ). These involve the terms: Me-Me (MM), Me-t-Bu (MB) and t-Bu-t-Bu (BB) at all four angles, together with a set of ten minor parameters, for a total of twenty two unknowns. The minor parameters, representing

interactions of Me groups relatively remote from one another, are evaluated first, by use of the Hill equation,<sup>3</sup> assuming that only C atoms contribute to the van der Waals interactions in these cases (Table 3). For the most part the values adopted were obtained by rounding the calculated values to the nearest 0.050 kcal. This allows assignment of potential energies to all of the systems shown in Chart 4 and reduces the number of unknowns to nine.

The conformational energy equation (Eq 7) is next used to establish relationships among the major parameters. This is done, essentially, by use of Eq 9e, which reduces to:

$$E_0 = \frac{E_{60} + E_{300}}{2} + \frac{E_{120} + E_{240}}{2} - E_{180}$$

By analysis of appropriate 1,2-disubstituted ethanes, 2, 3, and 4, we obtain the relationships:

$$MM_0 = MM_{60} + MM_{120} + 2.25 \quad (10a)$$

$$MB_0 = MB_{60} + MB_{120} + 2.95 \quad (10b)$$

$$BB_0 = BB_{60} + BB_{120} + 3.75 \quad (10c)$$

In a similar analysis of systems with two *gauche* Et groups, e.g. 5, it is found that:

$$X = \frac{BB_0 - MB_0}{2} + a - b + y - z$$

$$= \frac{BB_0 - MB_0}{2} - 0.075 \quad (11)$$

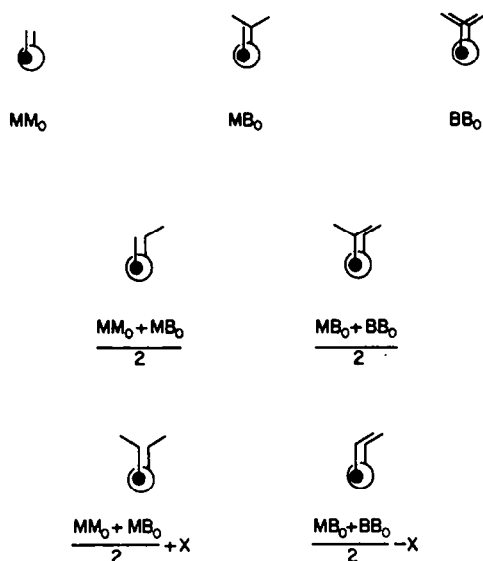
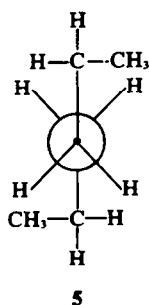
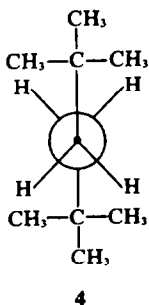
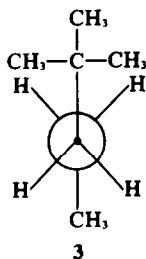
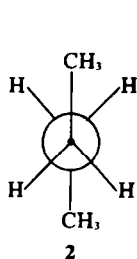


Chart 1. Group interactions where  $\gamma = 0^\circ$ . M = methyl; B = *t*-butyl.

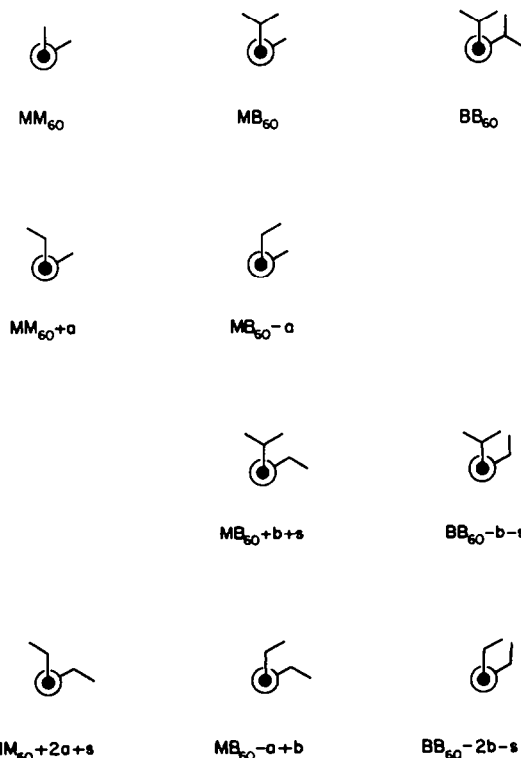


Chart 2. Group interactions where  $\gamma = 60^\circ$ . For the significance of parameters a, b and s, see Table 3.

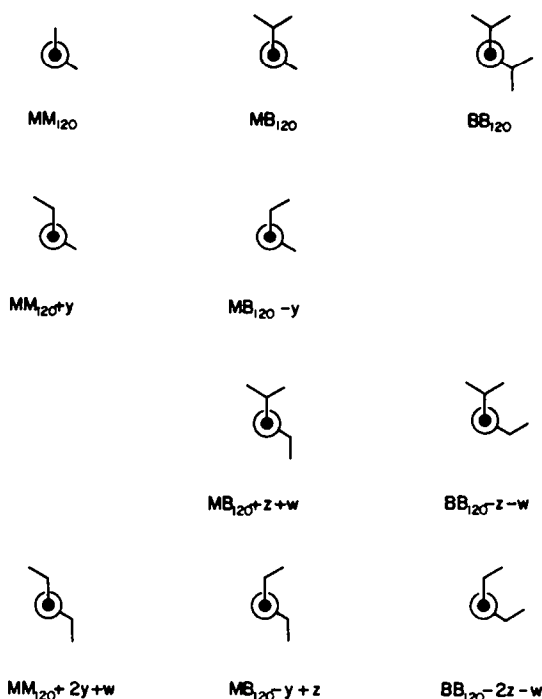
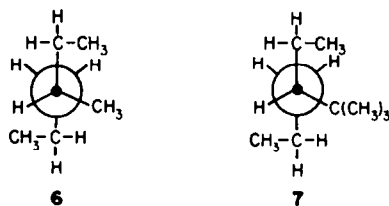


Chart 3. Group interactions where  $\gamma = 120^\circ$ . For the significance of parameters  $w$ ,  $y$  and  $z$ , see Table 3.

The trisubstituted systems, 6 and 7, give the additional relationships shown in Eqs 12a and 12b.



$$(MB_{60} - MM_{60}) - (MB_{120} - MM_{120}) = 2(a - y) \quad (12a)$$

$$(BB_{60} - MB_{60}) - (BB_{120} - MB_{120}) = 2(b + s - z - w) \quad (12b)$$

In cyclohexane systems, a 1,3-diaxial Me-Me interaction has been evaluated at 3.70 kcal/mol and the corresponding H-Me interaction as 0.90 kcal/mol.<sup>4</sup> Using these values, the change in conformational energy on the substitution 8  $\rightarrow$  9 should be worth 2.80 kcal/mol, whence:

$$MB_{60} - a = MM_{60} + 2.80$$

and

$$MB_{60} = MM_{60} + 2.675 \quad (13a)$$

$$MB_{120} = MM_{120} + 2.825 \quad (13b)$$

$$MB_0 = MM_0 + 6.200 \quad (13c)$$

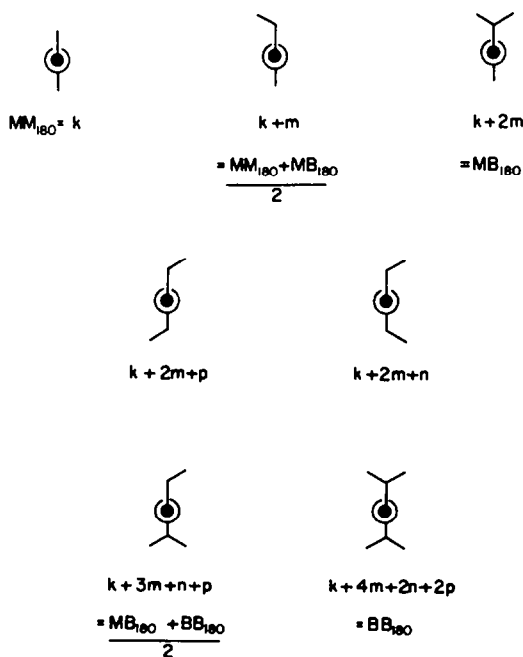
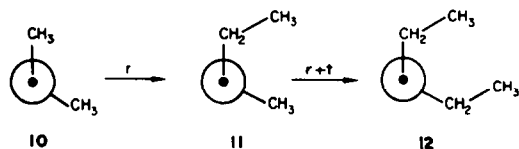


Chart 4. Group interactions where  $\gamma = 180^\circ$ . For the significance of parameters  $k$ ,  $m$ ,  $n$ , and  $p$ , see Table 3.



The corresponding substitution in the series where  $\gamma = 120^\circ$  can also be evaluated. The entering Me group should produce the change in potential energy:  $r = MB_{120} - y - MM_{120}$  in the substitutions 10  $\rightarrow$  11 and 11  $\rightarrow$  12, with an additional change,  $t$ , in the last step due to the interactions of the Me groups in 12. These Me groups are as close together



as those in 8 and are, furthermore, aimed toward one another (unlike the first entry in Table 3, where the carbon atoms are also this close). We assume, then, that the term  $t$  has the value:  $MM_{60}$ , whence:

$$BB_{120} - 2z - w = 2(MB_{120} - y) - MM_{120} + MM_{60} \quad (14)$$

or,

$$BB_{120} = MB_{120} + MM_{60} + 2.80 - a + 2z + w \quad (15)$$

Table 3. Interactions between relatively remote methyl groups

System	Symbol	C-C Distance Bond lengths	Å	Potential energy (kcal/mol) Calculated	Adopted
	b-a	$\sqrt{33}/3$	2.949	0.110	0.125
	a	$\sqrt{48}/3$	3.557	-0.124	-0.125
	MM <sub>120</sub>	$\sqrt{49}/3$	3.593	-0.121	-0.10
	MM <sub>180</sub>	$\sqrt{57}/3$	3.876	-0.093	-0.10
	y	$\sqrt{72}/3$	4.356	-0.052	-0.05
	m	$\sqrt{72}/3$	4.356	-0.052	-0.05
	s	$\sqrt{81}/3$	4.620	-0.037	-0.05
	z-y	$\sqrt{81}/3$	4.620	-0.037	-0.05
	n	$\sqrt{81}/3$	4.620	-0.037	-0.05
	p	$\sqrt{105}/3$	5.260	-0.018	0
	w	$\sqrt{105}/3$	5.260	-0.018	0

and

$$BB_{60} = MB_{60} + MM_{60} + 2.80 - a + 2b + 2s - w \quad (16)$$

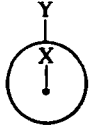
It is now possible to solve for all of the major terms by use of the value:  $MM_{60} = 0.70$  kcal/mol. This value is 0.80 kcal/mol larger than that for  $MM_{180}$ , consistent with the average of those obtained recently by NMR:  $0.681 \pm 0.035$  kcal/mol for n-butane<sup>5</sup> and  $0.888 \pm 0.018$  kcal/mol for isopentane.<sup>6</sup> The results so obtained are presented in Table 4. These values have been used to obtain the parameters for Eq 7 as it applies to a number of systems and these equations used in turn to calculate the population factors for the conformational septets shown in Table













5. These values are, in turn, used in the conformational analysis required for method IC. The conformational analysis used in method IB, on the other hand, makes use of the conformational energies for individual exactly staggered conformations, as computed from the values found in Table 4.

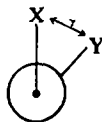
#### MOLECULAR ROTATION CONTRIBUTIONS

Elaborating upon a suggestion of Whiffen's,<sup>7</sup> we have proposed<sup>2</sup> that the molecular rotatory contribution of a twisted chain of four atoms, 13, should be positive in the *P* conformation and should have a magnitude depending upon constants characteristic of the terminal atoms, X and Y. We proposed then that this contribution should depend

Table 4. Partial conformational energies (kcal/mol)



X	Y	$\gamma = 0^\circ$	$60^\circ$	$120^\circ$	$180^\circ$	$240^\circ$	$300^\circ$
H	H	0.95					
H	CH <sub>3</sub>	1.55					
H		1.85					
H		2.15					
CH <sub>3</sub>	CH <sub>3</sub>	2.85	0.70	-0.10	-0.10	-0.10	0.70
CH <sub>3</sub>		5.95	3.50	2.775	-0.15	-0.15	0.575
CH <sub>3</sub>		9.05	3.375	2.725	-0.20	2.725	3.375
		9.125	3.50	2.675	-0.20	2.675	3.50
		9.75	6.95	6.35	-0.25	-0.20	0.40
		12.925	6.95	6.25	-0.30	2.625	3.325
		16.80	6.90	6.15	-0.40	6.15	6.90



$$\Delta[M]_D = + \sin \gamma k_x k_y$$

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upon the sine of the torsion angle  $\gamma$ . In several subsequent papers<sup>1,8,9</sup> we have shown that such a relationship is to be expected for systems whose chief response to light is a concerted perturbation of all the electrons along a chain of bonds—the Helical Conductor Model. It is a consequence of this latter model that significant rotatory contributions are to be expected from longer twisted chains of atoms as well, in accord with the expression:

$$\Delta[M]_D = 652 \frac{LA}{D^2} \bar{R}_A f(n) \quad (17)$$

In this model<sup>1,8,9</sup> the twisted chain is regarded as a single turn of a helix, with  $L$  the length of the helix axis,  $D$  the length of the bond system,  $A$  the area of the cross section of the helix (in a plane perpendicular to the axis),  $\bar{R}_A$  the average refraction of the bonds,<sup>1</sup> and  $f(n)$  a function of the refractive index

\*This equation can be transformed into one showing Drude-type dependence of  $\Delta[M]$  on the wavelength of light<sup>8</sup> and, so, adequately accounts for *rotatory dispersion* effects due to this particular kind of chromophore.

of the total solution.\* This Helical Conductor Model<sup>8</sup> subsumes and extends the original Conformational Dissymmetry Model,<sup>2</sup> but results in enough differences that productive tests may be possible.

The original four atom model (13) as used in method IA, has the particular merit that it can be applied easily across the board to even very complex substances.<sup>2,10</sup> Thus, the rotatory contributions of such four atom units to twisted paraffinic chains of 4, 5 and 6 members are, as shown in Table 6, simple multiples of  $\pm \sqrt{3}K/2$ , where  $K$  is the rotation of the unit 13 when  $\gamma = 90^\circ$ . In method IB, a refined version of IA, where conformer populations are assigned, not all-or-none, but rather on the basis of the energies of exactly staggered conformers (using the values in Table 4), we have retained this method of assigning rotatory contributions; this model, then, could be as widely applicable as the first. The Sept Dissymmetry Model (IC) is also, basically, a refinement of the first model, differing in the method for calculating both population probability factors and rotatory contributions, but still focussing on the four atom system 13. The rotatory contributions of septs are calculated thus:

$$\Delta[M]_D = \frac{\sum_{\gamma=-60^\circ}^{+60^\circ} K_{XY} \sin \gamma e^{-E_\gamma/RT}}{\sum_{\gamma=-60^\circ}^{+60^\circ} e^{-E_\gamma/RT}} \quad (18)$$

Values obtained in this way for a variety of paraffinic septs are shown in Table 5 (in parentheses). As

Table 5a. Population factors and rotations of conformational septs containing no more than one gauche ethyl group

$\gamma = 0^\circ-120^\circ$		$\gamma = 120^\circ-240^\circ$		$\gamma = 240^\circ-360^\circ$	
	8.8320 (+0.8627)		32.6820 0		8.8320 (-0.8627)
	9.7681 (-0.8345)		2.5700 0		9.7681 (+0.8345)
	0.9268 (+0.8633)		3.4474 0		0.9268 (-0.8633)
	$6.9433 \times 10^{-2}$ (+0.8624)		33.1820 (-0.0775)		10.6340 (-0.8988)
	9.9404 (-0.8497)		$2.4607 \times 10^{-2}$ (-0.0690)		$8.6661 \times 10^{-2}$ (+0.8105)
	11.8340 (-0.8047)		$2.0449 \times 10^{-2}$ (-0.0023)		10.5190 (+0.8033)
	$7.7848 \times 10^{-2}$ (-0.8417)		2.9411 (+0.0743)		9.3817 (+0.8798)
	$8.2066 \times 10^{-3}$ (+0.8942)		3.5562 (-0.0015)		$9.3559 \times 10^{-3}$ (-0.8949)
	0.9389 (+0.8641)		$2.9317 \times 10^{-2}$ (+0.0632)		$8.4241 \times 10^{-3}$ (-0.8302)

seen in Table 6,  $[M]_D$  values calculated in this way for particular twisted paraffin chains are similar to, but do differ somewhat from those used in methods IA and IB. Method IC is, in principle, the soundest version of the four atom model, but it requires the preparation of extensive Tables such as 5 and so would not appear to be as useful. The values shown in Table 6 indicate that not much is changed by calculating rotatory contributions by use of Eq 18; this point is also made in Table 7, in which comparisons of calculations of the rotation of (S)-3-

methylhexane by several methods are made. It is also seen in Table 7 that calculations of conformational population factors by use of Eq 2b give results that do not differ greatly from those obtained by use of Eqs 3a and 2a (method IB). Thus method IB would appear, in general, to be an adequate approximation to the more involved method IC. It is to be noted that both method IB and method IC also permit estimates to be made of the effect of temperature on optical rotation (see Eq 3). The remaining column in Table 6 shows, for comparison,



Table 5b. Population factors and rotations of conformational septs containing two gauche ethyl groups

$\gamma = 0^\circ-120^\circ$		$\gamma = 120^\circ-240^\circ$		$\gamma = 240^\circ-360^\circ$	
	$6.9515 \times 10^{-2}$ (+0.8956)		28.5470 0		$6.9515 \times 10^{-2}$ (-0.8956)
	$9.8808 \times 10^{-2}$ (-0.7902)		$1.6415 \times 10^{-4}$ (+0.0617)		10.8400 (+0.8272)
	$7.3261 \times 10^{-2}$ (-0.8514)		$1.9950 \times 10^{-2}$ (-0.0009)		$6.7440 \times 10^{-2}$ (+0.8509)
	$1.8286 \times 10^{-4}$ (+0.8624)		44.9300 (-0.1263)		16.6890 (-0.9188)
	13.4690 (-0.8239)		$6.6074 \times 10^{-3}$ (-0.0595)		0.1200 (+0.7880)
	11.0290 (-0.8806)		$3.7157 \times 10^{-2}$ (-0.1138)		$2.2945 \times 10^{-4}$ (+0.8205)
	$7.6732 \times 10^{-2}$ (-0.8789)		2.8787 0		$7.6732 \times 10^{-2}$ (+0.8789)
	9.7198 (-0.8504)		$2.3854 \times 10^{-2}$ (-0.0652)		$8.3882 \times 10^{-2}$ (+0.8137)
	14.5150 (-0.7855)		$1.6557 \times 10^{-4}$ 0		14.5150 (+0.7855)

the rotations calculated for the same twisted chains by use of the Helical Conductor Model.<sup>1</sup> In a number of cases these values differ not only in magnitude but in sign, offering the possibility of a test of these differences. One such test, involving the highly symmetrical and rigid substance, twistane,<sup>11</sup> gave calculated rotations of opposite sign with the the two methods; current evidence on the configuration of twistane<sup>11</sup> indicates that it is the Helical Conductor Model that gives the correct result.

We have calculated rotations for a number of

paraffinic hydrocarbons by these various methods. In Table 7 are shown results for (*S*)-3-methylhexane, which has three conformationally significant bonds. Under method IA only 6 of the 27 conformers are "allowed" and they are given equal weight; their  $[M]_D$  contributions are multiples of 60° (from Table 6;  $K = 69^\circ$ ). This method gives a good rotation value (+10°; observed, 9.9°). The conformer population calculated from energies of exactly staggered conformers—and omitting those conformers present to an extent of less than 0.5%

Table 5c. Population factors and rotations of conformational septs containing isopropyl or t-butyl groups

$\gamma = 0^\circ-120^\circ$		$\gamma = 120^\circ-240^\circ$		$\gamma = 240^\circ-360^\circ$	
	$8.3950 \times 10^{-2}$ (+0.8938)		28.3900 0		$8.3950 \times 10^{-2}$ (-0.8938)
	$9.1223 \times 10^{-2}$ (-0.8308)		$2.0849 \times 10^{-4}$ 0		$9.1223 \times 10^{-2}$ (+0.8308)
	$9.4487 \times 10^{-2}$ (-0.8149)		$2.3634 \times 10^{-2}$ (+0.0618)		8.5836 (+0.8496)
	$8.6136 \times 10^{-3}$ (+0.8851)		$3.1642 \times 10^{-2}$ (+0.0414)		$7.5468 \times 10^{-3}$ (-0.8651)
	$1.8289 \times 10^{-4}$ (+0.8908)		32.9830 (-0.0567)		0.1085 (-0.9147)
	0.1136 (-0.8109)		$4.7073 \times 10^{-2}$ (+0.0008)		0.1229 (+0.8114)
	$8.9564 \times 10^{-2}$ (-0.8607)		$2.2415 \times 10^{-4}$ (-0.0502)		$2.0565 \times 10^{-4}$ (+0.8339)
	10.4110 (-0.8599)		$2.4676 \times 10^{-4}$ (-0.1040)		$2.5792 \times 10^{-4}$ (+0.8016)
	$2.1632 \times 10^{-2}$ (-0.8271)		$5.5022 \times 10^{-3}$ (-0.0004)		$8.8020 \times 10^{-2}$ (+0.8269)
	$2.3368 \times 10^{-4}$ (+0.9103)		32.1060 0		$2.3367 \times 10^{-4}$ (-0.9103)
	$2.5409 \times 10^{-4}$ (-0.8155)		$5.0814 \times 10^{-7}$ (+0.04631)		0.1048 (+0.8416)

Table 6. Rotatory contributions of twisted paraffinic chains:  $\text{CH}_2(\text{CH}_2)_n\text{CH}_3$ 

n	Conformer*	IC	$\Delta M_D/K^\dagger$	
			Method of Calculation IA, IB	Helix Model (Ref 1)
2	<i>P</i>	+0.8627	+0.8660	+0.8660
3	<i>TT</i>	0	0	0
	<i>PT</i>	+0.9402	+0.8660	0
	<i>PP</i>	+1.7977	+1.7320	1.9500
4	<i>PM</i>	0	0	0
	<i>TTT</i>	0	0	0
	<i>PTT</i>	+0.9402	+0.8660	+0.6232
	<i>TPT</i>	+1.0177	+0.8660	-0.3110
	<i>PPT</i>	+1.8752	+1.7320	+0.9366
	<i>PTP</i>	+1.8516	+1.7320	-0.9366
	<i>PPP</i>	+2.7165	+2.5980	+2.1842
	<i>PMT</i>	-0.0775	0	+0.6232
	<i>PTM</i>	0	0	0
	<i>MPP</i>	+0.9320	+0.8660	+1.5524
	<i>PMP</i>	+0.8625	+0.8660	+0.6232

\*For the meaning of *P*, *M* and *T*, see Fig 1. *n*-Hexane (*n* = 4) has three conformationally significant bonds, requiring the use of three symbols (e.g., *TTT*) for definition.

†K is the value for  $\Delta M_D$  when  $\gamma = 90^\circ$ .

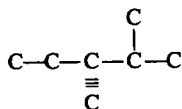
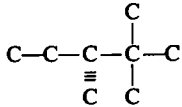
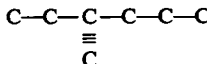
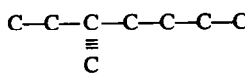
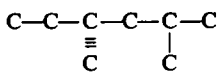
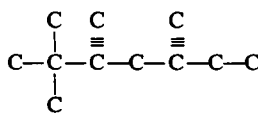
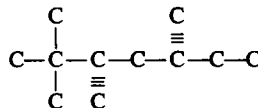
Table 7. Comparison of methods for conformational analysis and for assigning conformer rotations for (*S*)-3-methylhexane

Conformer	Conformer fraction			Conformer rotation		
	1A	1B	1C	1A, 1B	1C	Helix
<i>TTT</i>	0.1667	0.1770	0.1904	0	-5.425	-51.96
<i>TTP</i>	0.1667	0.0566	0.0610	+60	+63.98	+102.43
<i>TM</i>			0.0004		-62.05	-89.35
<i>PTT</i>	0.1667	0.1926	0.1904	+120	+125.49	+37.39
<i>PTP</i>	0.1667	0.0670	0.0610	+180	+178.67	+60.80
<i>PTM</i>			0.0004		+57.61	0
<i>MTT</i>		0.0499	0.0502	+60	+61.66	+14.57
<i>MTP</i>		0.0160	0.0161	+120	+120.82	+168.96
<i>MTM</i>			0.0001		-4.87	+108.16
<i>TMT</i>	0.1667	0.1926	0.1904	-120	-122.26	-33.30
<i>TMP</i>			0.0004		-54.78	-14.57
<i>TMM</i>	0.1667	0.0616	0.0610	-180	-180.81	-108.16
<i>PMT</i>		0.0016	0.0015	0	-5.43	+37.33
<i>PMP</i>			0		+61.95	+37.33
<i>PMM</i>			0.0004		-63.60	-93.14
<i>MMT</i>		0.0566	0.0573	-60	-66.96	-4.24
<i>MMP</i>			0.0001		-0.15	-41.18
<i>MMM</i>		0.0243	0.0200	-120	-115.75	-79.09
<i>TPT</i>		0.0543	0.0462	-60	-56.23	-70.62
<i>TPP</i>			0.0001		+11.17	+4.94
<i>TPM</i>			0.0001		-123.63	-240.74
<i>PPT</i>		0.0499	0.0519	+60	+61.53	+65.56
<i>PPP</i>			0.0002		+126.23	+152.89
<i>PPM</i>			0		-6.30	-27.83
<i>MPT</i>			0.0009		0	+17.00
<i>MPP</i>			0		+66.89	+145.10
<i>MPM</i>			0		-62.57	-102.43

(method IB) are quite similar to those calculated by the sept method (IC). The rotatory contributions calculated by the helix model are seen to be generally different from the others. It is, therefore, of

interest that these values also lead to a good rotation for this substance (+8.7°), while the various refinements of the original conformational dissymmetry model do not do so well.

Table 8. Molecular rotations of some paraffinic hydrocarbons

Substance	Conformers "Allowed"		IA*	[M] <sub>b</sub> <sup>25</sup> Calculated			Observed	Reference
	IA	IB		IB	IC	Helix†		
	1	6	-60	-24.5	-26.3	-6.07	-11.1	a
	1	2	-60	-60	-58.1	-51.2	-49.8	a
	6	13	+10	+2.7	+5.06	+8.7	+9.9	b
	15	26	+12	+5.4	+10.2		+11.4	b
	3	5	+19.9	+13.2	+20.7	+25.7	+22.9	b
	1	11	-180	-159.7	-160.5		-97.5	c
	2	5	+120	+121.2	+117.2		+137.8	c

\*K = 70

†K = 60

\*L. Lardicci, R. Menicagli, A. M. Caporusso and G. Giacomelli, *Chemistry and Industry* (London) 184 (1963).\*R. E. Marker, *J. Am. Chem. Soc.* 58, 976 (1936).\*Cited in P. Pino, F. Ciardelli and M. Zandomenighi, *Rev. Phys. Chem.* 21, 561 (1970).

A comparison of the four methods for calculating rotations for flexible hydrocarbons is also shown Table 8. The original, all-or-none approach (method IA) does best in cases where three or more conformers are "allowed". The more inclusive methods, IB and IC, give generally comparable results, with a significant improvement for the case of *S*-2,3-dimethylpentane, but a worsening for (*S*)-3-methylhexane and (*S*)-3-methylheptane. The helix model, using the conformational analysis scheme of method IB, but using rotation values for chains of 4, 5 and 6 atoms (Table 6) gives generally acceptable results for those compounds to which it can presently be applied (substances with chains no longer than seven members). This suggests that it remains the most promising of all the methods considered here.

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