

Semiempirical Calculation of Conformational Structure of 2,4-Disubstituted Pentanes

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Abstract

The conformational structure of a series of 2,4-disubstituted pentanes (substituents F, Cl, Br, I, CN, CH₃, H) has been calculated, taking account of three types of interactions: dispersion interactions, dipole-dipole interactions, and the three-fold barrier of the C-C bond. Dihedral angles have been adjusted so as to attain the local potential energy minimum for each conformer. The results of these calculations indicate the presence of a number of minority conformers, in addition to those considered previously.

Keywords: Stereo-conformations, Conformational calculations, Molecular dynamics

SEMIEMPIRICAL CALCULATION OF CONFORMATIONAL STRUCTURE OF 2,4-DISUBSTITUTED PENTANES

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The conformational structure of a series of 2,4-disubstituted pentanes (substituents F, Cl, Br, I, CN, CH₃, H) has been calculated, taking account of three types of interactions: dispersion interactions, dipole-dipole interactions, and the three-fold barrier of the C—C bond. Dihedral angles have been adjusted so as to attain the local potential energy minimum for each conformer. The results of these calculations indicate the presence of a number of minority conformers, in addition to those considered previously.

2,4-Disubstituted pentanes are important as dimer models of the corresponding vinyl polymers, and their conformational structure has been the subject of several studies¹⁻⁵. Except for 2,4-dimethylpentane, all these compounds exist in the form of two stereoisomers, (\pm) and *meso*, corresponding to the syndiotactic and isotactic diad of the polymer.

Older ideas⁴ about the conformational structure of vinyl polymers and their models were based on the assumption about the validity of the "staggered" approximation, with all dihedral angles of the C—C chain limited to values corresponding to the staggered form of the ethane molecule. In this approximation the conformation of the 2,4-disubstituted pentane is designated⁶ by two symbols, describing the dihedral angles of the central C₂C₃ and C₃C₄ bonds. The symbol T is used to describe the *trans* conformation of the chain, the symbols G and \bar{G} to describe the *gauche* conformations (Fig. 1).

Analysis of experimental data has shown¹⁻⁴ that the main features of infrared and NMR spectra of most 2,4-disubstituted pentanes can be interpreted assuming the presence of conformers TT and GG in the (\pm)-isomer, and of conformer TG in the *meso*-isomer. The TT conformer has been proved to be more stable than GG in (\pm)-2,4-dichloropentane¹, and in the other models the relative conformer stability was assumed to be similar. These considerations were also confirmed by theoretical calculations of McMahon⁷ who has calculated the contribution of Lennard-Jones type non-bonded interactions for all conformers of (\pm)- and *meso*-isomers of a series of 2,4-disubstituted pentanes in the staggered approximation. According to these calculations, the TT and GG conformers in the (\pm)-isomer, and the TG conformer in the *meso*-isomer are the only forms that can be expected to occur in measurable quantities.

However, recent results⁵ of detailed analysis of infrared and NMR spectra of both isomers of 2,4-dichloropentane indicate that the situation is much more complicated. Both in the (\pm)-

and in the *meso*-isomer, small amounts of additional conformers have been detected; the existence of these forms was excluded by McMahon's calculations⁷, but their presence could explain some discrepancies between interpretations of older spectral data and relatively small values of end-to-end distances in isotactic polymers. The existence of these conformers indicates that the staggered approximation is not adequate for the description of the conformational structure of linear molecules. This is in agreement with the papers by Abe, Jernigan and Flory⁸ and by Scott and Scheraga⁹ about the conformational structure of linear hydrocarbons and polyethylene, revealing the existence of large deviations of dihedral angles from staggered values.

In this paper, the conformational structure of a series of 2,4-disubstituted pentanes ($R = F, Cl, Br, I, CN, H, CH_3$) has been calculated. Dihedral angles have not been fixed to staggered values, but were adjusted so as to attain a minimum of the potential energy value.

THEORETICAL

If the conformation of a molecule is determined by n parameters, then the potential energy can be described as a surface in $(n + 1)$ dimensional space. Stable conformers of the molecule correspond to local minima on this surface. In a semiempirical approach the relation between the potential energy of a molecule and its geometrical structure can be defined by a number of factors; in acyclic molecules, the most important of these are: 1. non-bonded interactions, 2. three-fold barriers of C—C bonds, 3. dipole-dipole interactions of polar bonds, and 4. intermolecular interactions.

Experimental data on 2,4-dichloropentane² indicate that its conformational structure remains practically the same in different solvents. Also on theoretical

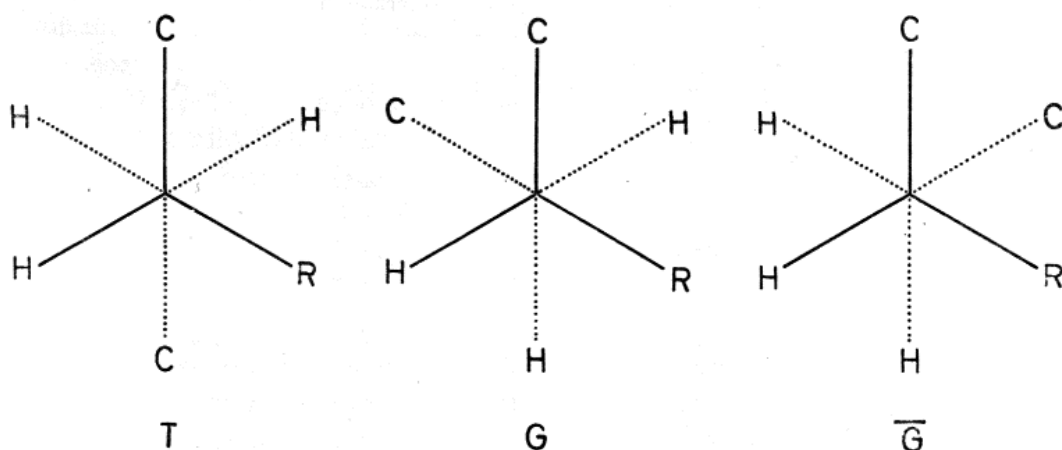


FIG. 1

Designation of Conformational Structures in Staggered Approximation

grounds¹⁰ it may be expected that for moderate values of dielectric constant of the medium for molecules of this size, the influence of surrounding medium will be small. Our considerations will therefore be limited to the first three types of interactions, and the potential energy will then be approximated by the relation

$$E = V_w + V_3 + V_e, \quad (1)$$

V_w designating the energy of non-bonded interactions of atoms, V_3 the contribution of the three-fold barriers of all C—C bonds, and V_e the contribution of bond dipole interactions.

Non-bonded interactions have in this paper been calculated by means of the Buckingham^{11,12} potential, with

$$V_w = \sum_{i,j} V_{ij}^w; \quad (2)$$

$$V_{ij}^w = A_{ij} \exp(-B_{ij}R_{ij}) - C_{ij}/R_{ij}^6, \quad (3)$$

with summation over all pairs of atoms not bound to each other or to a common atom. R_{ij} is the distance of atoms i, j and A_{ij} , B_{ij} , C_{ij} are semiempirical constants depending on the type of the atoms, i, j . These constants have been determined by the procedure suggested by Pitzer¹³ and by Scott and Scheraga¹⁴. C_{ij} was calculated from the Slater-Kirkwood equation

$$C_{ij} = 362 \cdot \alpha_i \alpha_j / (\sqrt{[\alpha_i/n_i]} + \sqrt{[\alpha_j/n_j]}), \quad (4)$$

TABLE I
Parameters Applied for the Determination of Dispersion Interaction Coefficients

Atom	n	$\alpha, 10^{-24}, \text{cm}^3$	$b, \text{\AA}^{-1}$	$r_w, \text{\AA}$
H	0.9	0.42	4.54	1.20
C	5.2	0.93	4.59	1.70
Cl	16.2	2.28	3.75	1.75
Br	21.9	3.34	3.04	1.85
J	30.0	5.05	2.92	2.06
F	8.0	0.60 ^a	4.60	1.47
C (CN)	5.2	1.09	4.59	1.78
N (CN)	6.0	1.03	4.57	1.60

^a Polarizabilities of methyl and ethylfluoride¹⁷ were used and additivity rule applied to obtain this value; n effective atomic number¹³, α polarizability¹⁶, b repulsion coefficient^{14,15}, r_w van der Waals radius¹⁸.

with α_i , α_j designating the polarizabilities of atoms i , j in units of 10^{-24} cm³ and n_i , n_j designating effective atomic numbers read off an empirical graph¹³. The parameters B_{ij} have been determined by means of Mason's¹⁵ combination rule

$$B_{ij} = (b_{ii} + b_{jj})/2 \quad (5)$$

with values b_{ii} read off empirical graphs¹⁴. The parameter A_{ij} has been determined so as to locate the minimum of the Buckingham potential at a distance equal to the sum of the van der Waals radii r_w of atoms i and j . The values of the basic parameters n , α , b , r_w for various atoms used in the calculation are given in Table I.

For very small values of R_{ij} the Buckingham potential is known to pass through a maximum. This maximum has no physical meaning and moreover interferes with the computational procedure applied. For this reason, potential (3) has only been used for values of $R_{ij} > Q_{ij}$, being substituted by relation

$$V_{ij}^w = D_{ij} \cdot R_{ij}^{-E_{ij}} \quad (6)$$

for values of $R_{ij} < Q_{ij}$ ¹⁹.

The coefficients D_{ij} and E_{ij} have been chosen so as to equalize the functional values and their first derivatives for both potentials (3) and (6) in the point $R_{ij} = Q_{ij}$. The value Q_{ij} has been chosen so as to obey the relation

$$Q_{ij} = R_{\text{inf}} + 0.4(R_{\text{min}} - R_{\text{inf}}) \quad (7)$$

where R_{min} and R_{inf} are the coordinates of the minimum and point of inflection of the Buckingham potential, respectively. Under these conditions the coefficients E_{ij} attain the value of about 8, in rough agreement with the average experimental value of this coefficient¹⁹. The value of Q_{ij} is actually rather inconsequential in very broad limits, as the potential (6) only becomes important in energetically unfavourable positions. The calculated values of parameters A_{ij} to Q_{ij} are given in Table II.

The three-fold barrier of the C—C bond of sp^3 — sp^3 type has been approximated by the relation

$$V_3 = \sum_k 1.5(1 + \cos 3\varphi_k) \quad (8)$$

with summation over all dihedral angles φ_k in the molecule.

For the calculation of dipole-dipole interactions, the bond dipole moments have been considered as point dipoles located in the centre of the corresponding bonds. Then

$$V_e = + \sum_{\alpha, \beta} \{ (\bar{m}_\alpha \cdot \bar{m}_\beta) / R_{\alpha\beta}^3 - 3(\bar{m}_\alpha \cdot \bar{R}_{\alpha\beta})(\bar{m}_\beta \cdot \bar{R}_{\alpha\beta}) / R_{\alpha\beta}^5 \} \quad (9)$$

with summation over all pairs (α, β) of polar bonds not originating from the same atom; \bar{m}_α and \bar{m}_β are vectors of the corresponding dipole moments and $\bar{R}_{\alpha\beta}$ is the vector connecting both dipoles. In the molecules treated in this paper, the summation includes at most one member.

Bond angles have in all cases been considered as tetrahedral, bond lengths and dipole moments are given in Table III.

All calculations have been performed on the Minsk 22 computer, with programmes written in the machine code of this computer. With these programmes it is possible to calculate the potential energy of the molecule according to relations (1) to (9), and to adjust dihedral angles to the nearest local minimum of potential energy by the steepest descent method.

TABLE II

Dispersion Interaction Coefficients for Various Pairs of Atoms

$$V = A \cdot \exp(-B \cdot r) - C/r^6 \text{ for } r > Q; V = D \cdot r^{-E} \text{ for } r < Q.$$

Interaction	$A \cdot 10^{-3}$	B	C	$D \cdot 10^{-2}$	E	Q
H...H	7.27	4.54	46.7	1.42	8.77	1.60
H...C	54.7	4.57	128	12.3	7.95	1.65
H...Cl	49.8	4.15	328	21.9	8.08	1.78
H...Br	32.0	3.79	473	28.4	8.30	1.93
H...J	55.1	3.73	702	56.7	8.09	1.98
H...F	25.8	4.57	95.3	5.14	8.08	1.62
H...C(CN)	74.0	4.57	145	17.3	7.94	1.66
H...N(CN)	48.2	4.55	143	10.5	7.99	1.64
C...C	552	4.59	370	156	8.12	1.74
C...Cl	421	4.17	962	222	7.98	1.85
C...Br	233	3.81	1 380	225	7.94	1.99
C...J	416	3.75	2 040	487	7.96	2.04
C...F	249	4.59	290	61.8	7.99	1.69
C...C(CN)	762	4.59	417	226	8.18	1.75
C...N(CN)	466	4.58	414	127	8.05	1.72
Cl...Cl	313	3.75	2 510	331	7.95	2.00
Br...Br	82.5	3.04	5 170	486	8.48	2.40
J...J	192	2.92	11 300	1 440	8.13	2.52
F...F	122	4.60	238	26.7	7.94	1.65
C(CN)...C(CN)	1 060	4.59	470	329	8.24	1.77
C(CN)...N(CN)	640	4.58	466	182	8.10	1.73
N(CN)...N(CN)	397	4.57	463	104	7.99	1.70

Energy unit: kcal/mol; unit of length: Å.

TABLE III
Bond Lengths²⁰ and Dipole Moments²¹ Used in Calculations

Bond	C—C	C—H	C—Cl	C—Br	C—J	C—F	C—CN	C≡N
Length, Å	1.53	1.10	1.76	1.91	2.28	1.42	1.49	1.16
Dipole moment, D	0	0	1.85	1.80	1.64	1.81	0	3.94

In this paper, for the molecules considered, 1) the values of potential energies of all conformers of the staggered approximation have been calculated, and 2) all stable conformers have been found together with the corresponding values of dihedral angles and energies E , V_w , V_3 , V_e . The term "stable conformer" will in the following be used to designate forms corresponding to local minima on the potential energy surface. Stable conformers will be designated by the same symbols as the nearest conformers of the staggered approximation: Precisely they are defined by the values of all dihedral angles (Fig. 2).

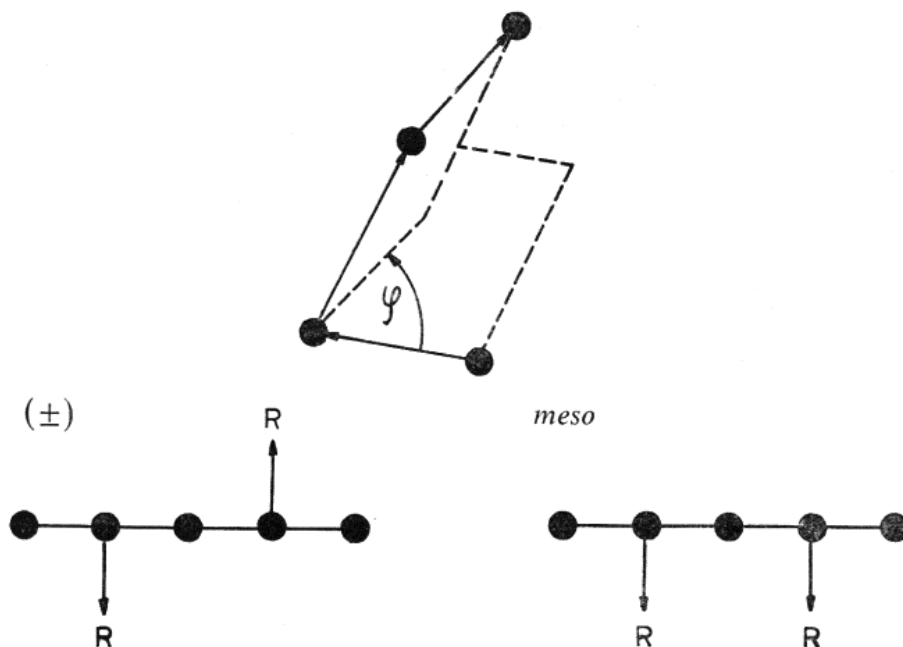


FIG. 2
Formalism Used to Determine Dihedral Angle Values

RESULTS AND DISCUSSION

2,4-Dichloropentane

The conformational structure of this molecule has been investigated experimentally in great detail¹⁻⁵. For a comparison of experimental and theoretical results, it will be worth while to consider first some qualitative facts following from the calculations.

The relative energies of stable conformers (Table IV *c, d*) differ in almost all cases very considerably from the values obtained by staggered approximation. In some cases (conformers TG, \overline{TG} , \overline{GG} , \overline{GG} in the (\pm)-isomer and \overline{GG} , \overline{GG} in the *meso*-isomer), two local potential energy minima (designated *a, b*) are found in the vicinity of a single conformer of the staggered approximation. This increases the number of possible conformers compared to the staggered approximation. Furthermore, some conformers (TT, GG, \overline{GG} in the *meso*-isomer and \overline{GG} in the (\pm)-isomer) have an unsymmetrical stable form corresponding to a symmetrical form in staggered approximation, increasing thus the statistical weight of the stable conformer.

From infrared and NMR spectra, the TT conformer is the most stable form of (\pm)-2,4-dichloropentane^{1,2}. In addition the presence of further three minor conformers⁵ has been proved in this isomer. Of these, the most favoured one is GG (energy relative to TT 2 kcal/mol), followed by TG (2.5 kcal/mol) and by \overline{GG} (present in very small amounts). These results are to be compared with the calculated values (Table IV*c*), yielding the following sequence (relative energies in kcal/mol given in brackets): *a) staggered approximation*: TT, GG (1.8), \overline{TG} (20.0), TG (40.5), \overline{GG} (80.3), \overline{GG} (3185); *b) stable conformers*: TT, GG (1.5), TG_b (2.5), TG_a (3.0), \overline{GG} _a (3.7), \overline{TG} _b (4.6), \overline{TG} _a (6.5), etc.

In *meso*-2,4-dichloropentane, the TG conformer has been found as the most stable one¹. In infrared spectra⁵, two additional lines have been observed in the region of CCl-stretching vibrations. One of these (645 cm⁻¹) indicates (rel. energy about 1.5 kcal/mol) the presence of some of the conformers \overline{TG} , TT, \overline{GG} or possibly \overline{GG} , whereas the other indicates the presence of a small amount of form GG. Calculations yielded the following data: *a) staggered approximation*: TG, TT (18.6), \overline{TG} (39.4), \overline{GG} (40.2), GG (3184), \overline{GG} (3203); *b) stable conformers*: TG, \overline{TG} (1.7), GG (2.8), TT (2.9), \overline{GG} _a (3.1), \overline{GG} _b (4.7), \overline{GG} (22.7).

The staggered approximation is thus seen to determine correctly the most stable conformer, but otherwise it proves quite unsuitable for a more detailed investigation of the conformational structure of the molecule. By adjustment of dihedral angles, a good agreement of theoretical and experimental data is seen to be obtained in both isomers.

All these facts together with the magnitude of deviations of optimum angles from staggered values lead to the conclusion that the conformer designation by means of the symbols T, G and \overline{G} does not have real physical significance, although it might remain useful for rough orientation.

2,4-Dihalosubstituted Pentanes

The results of conformer energy calculations for 2,4-difluoro-, dibromo-, and diiodopentane are given in Table IVa, b, e–h, and summarized in Fig. 3. Interesting is the decreasing trend of the relative energy of the GG conformer in the (\pm)-isomer with increasing volume of the halogen atom. Such a trend has been observed by McMahon and Tincher³ for R = Cl, Br. In *d,l*-2,4-difluoropentane, the stability of the GG conformer decreases below that of TG. A similar trend may be observed in the GG conformers in the *meso*-isomers. From Fig. 3 it may also be seen that the occurrence of two energy minima in the vicinity of one staggered form is frequent for Cl and Br derivatives, but does not occur with very small (F) or very large (I) substituents.

The applied empirical model should be capable of reproducing correctly also the difference of enthalpy between the two major forms in the isomers ("configuration energy" $E_k = E_{TG}(meso) - E_{TT}(\pm)$). From Table IV the values of E_k are seen to decrease in the series F (0,86 kcal/mol), Cl (0,72), Br (0,63), I (0,52).

2,4-Dicyanopentane

The large dipole moment of the group CN causes the 2,4-dicyanopentane to differ considerably from the 2,4-dihalosubstituted pentanes. This is in itself surprising, because it has been assumed so far⁴ that the conformational structure of both isomers of this compound is similar to that of 2,4-dichloropentane.

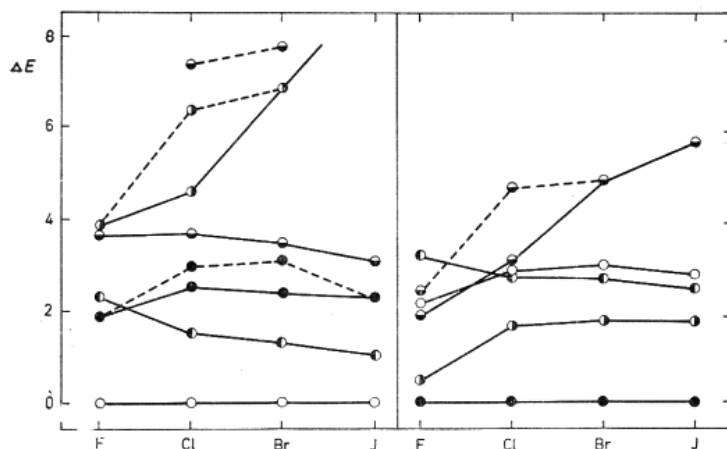


FIG. 3

Relative Conformer Energies in a) (\pm)- and b) *meso*-Isomers of 2,4-Dihalosubstituted Pentanes
Designation of Conformers: \circ TT, \bullet TG, \bullet TĠ, \circ GG, \bullet GĠ.

TABLE IV
Energy and Structure of Stable Conformers of 2,4-Disubstituted Pentanes

Conformer	<i>k</i>	<i>V_w</i>	<i>V_e</i>	<i>V₃</i>	Total energy		<i>E_{stg}</i>	Dihedral angles			
					abs	rel		C ₁ C ₂	C ₂ C ₃	C ₃ C ₄	C ₄ C ₅
<i>a) (±)-2,4-difluoropentane</i>											
TT	1	-4.84	0.04	0	-4.79	0	0	181	180	181	180
TG	2	-4.44	0.80	0.79	-2.85	1.9	7.6	190	-72	192	180
T \bar{G}	2	-4.24	2.76	0.47	-1.01	3.8	4.1	173	68	191	180
GG	1	-4.36	1.61	0.27	-2.48	2.3	2.8	188	-61	-61	188
G \bar{G} a	2	-4.51	0.97	2.42	-1.12	3.7	3 185	179	-100	64	172
G \bar{G} b	2	-3.47	0.03	2.39	-1.05	3.7	3 185	190	-66	98	180
$\bar{G}\bar{G}$ a	1	-0.35	0.07	1.11	0.84	5.6	13.7	164	53	53	164
$\bar{G}\bar{G}$ b	1	-1.73	1.19	2.18	1.65	6.4	13.7	177	85	85	177
<i>b) meso-2,4-difluoropentane</i>											
TT	1	-4.81	2.73	0.23	-1.85	2.1	2.1	180	188	172	180
TG	2	-4.66	0.58	0.15	-3.93	0	0	185	-64	186	180
T \bar{G}	2	-4.30	0.05	0.79	-3.46	0.5	5.7	170	65	163	180
GG	2	-4.75	1.55	2.47	-0.73	3.2	3 185	179	-101	64	173
G \bar{G} a	2	-4.04	0.27	1.87	-1.90	2.0	6.8	181	-90	-73	182
G \bar{G} b	2	-3.25	0.79	0.91	-1.55	2.4	6.8	168	51	65	165
$\bar{G}\bar{G}$	2	-1.54	2.65	2.23	3.33	7.3	3 187	171	58	-97	181
<i>c) (±)-2,4-dichloropentane</i>											
TT	1	-6.30	0.36	0.10	-5.84	0	0	180	185	185	180
TG a	2	-5.95	0.68	2.45	-2.82	3.0	40.5	181	-102	186	180
TG b	2	-6.10	1.04	1.69	-3.37	2.5	40.5	181	209	-67	180
T \bar{G} a	2	-3.09	2.44	1.25	0.60	6.4	20.0	168	39	190	180
T \bar{G} b	2	-5.42	1.65	2.57	-1.20	4.6	20.0	181	222	68	176
GG	1	-5.92	1.36	0.25	-4.30	1.5	1.8	188	-61	-61	188
G \bar{G} a	2	-5.66	1.08	2.40	-2.18	3.7	3 185	180	-101	58	174
G \bar{G} b	2	-1.75	0.42	2.90	1.57	7.4	3 185	203	-64	85	159
$\bar{G}\bar{G}$ a	1	13.90	0.44	1.07	15.42	21.3	80.3	170	47	47	170
$\bar{G}\bar{G}$ b	2	13.00	1.20	5.10	19.31	25.2	80.3	182	91	77	120
<i>d) meso-2,4-dichloropentane</i>											
TT	2	-6.13	2.22	1.67	-2.25	2.9	18.6	181	208	168	180
TG	2	-6.03	0.78	0.13	-5.12	0	0	187	-64	179	180
T \bar{G}	2	-5.67	0.47	1.78	-3.42	1.7	39.4	172	57	148	180
GG	2	-6.12	1.34	2.45	-2.34	2.8	3 184	179	-101	64	173
G \bar{G} a	2	-5.44	0.52	2.89	-2.04	3.1	40.2	179	-110	-66	183
G \bar{G} b	2	-3.22	0.94	1.66	-0.61	4.7	40.2	168	40	68	163
$\bar{G}\bar{G}$	2	11.23	2.42	3.90	17.56	22.7	3 203	169	42	-78	223

TABLE IV
(Continued)

Conformer	<i>k</i>	<i>V_w</i>	<i>V_e</i>	<i>V₃</i>	Total energy		<i>E_{stg}</i>	Dihedral angles			
					abs	rel		C ₁ C ₂	C ₂ C ₃	C ₃ C ₄	C ₄ C ₅
e) (±)-2,4-dibromopentane											
TT	1	-6.90	0.44	0.13	-6.33	0	0	180	186	186	180
TG a	2	-6.57	0.64	2.70	-3.22	3.1	48.0	180	-106	186	180
TG b	2	-6.69	0.95	1.83	-3.91	2.4	48.0	181	211	-66	189
T \bar{G}	2	-3.01	2.16	1.46	0.61	6.9	23.5	169	37	191	180
GG	1	-6.40	1.16	0.25	-4.99	1.3	1.6	188	-61	-61	188
G \bar{G} a	2	-6.30	1.00	2.43	-2.88	3.5	3 185	179	-102	58	174
G \bar{G} b	2	-2.20	0.48	3.15	1.44	7.8	3 185	155	82	-66	205
$\bar{G}\bar{G}$ a	1	16.28	0.51	0.93	17.72	24.1	95.3	174	46	46	172
$\bar{G}\bar{G}$ b	2	18.25	1.13	5.35	24.74	31.1	95.3	218	86	81	206
f) meso-2,4-dibromopentane											
TT	2	-6.68	1.83	2.11	-2.74	3.0	22.3	180	188	144	179
TG	2	-6.59	0.74	0.14	-5.70	0	0	187	-64	178	180
T \bar{G}	2	-6.34	0.52	1.92	-3.91	1.8	47.0	181	-146	-57	187
GG	2	-6.61	1.15	2.45	-3.01	2.7	3 184	179	-101	64	173
G \bar{G}	2	-3.42	0.87	1.74	-0.81	4.9	47.7	169	39	68	164
$\bar{G}\bar{G}$	2	13.07	2.22	3.92	19.21	24.9	3 206	171	41	-77	224
g) (±)-2,4-diiodopentane											
TT	1	-7.25	0.50	0.23	-6.52	0	0	180	187	187	180
TG	2	-6.98	0.70	2.03	-4.25	2.3	85.6	187	-65	215	180
T \bar{G}	2	-1.19	1.46	2.18	2.45	9.0	86.8	173	27	193	180
GG	1	-6.52	0.78	0.26	-5.49	1.0	0.9	188	-62	-62	188
G \bar{G}	2	-6.72	0.77	2.48	-3.47	3.1	3 184	180	-102	57	174
GG a	1	23.69	0.52	1.04	25.25	31.8	171	181	44	44	181
$\bar{G}\bar{G}$ b	1	26.58	0.92	7.68	35.18	41.7	171	233	83	83	233
h) meso-2,4-diiodopentane											
TT	2	-7.22	1.08	2.96	-3.18	2.8	85.9	180	185	127	180
TG	2	-6.83	0.61	0.21	-6.00	0	0	187	-66	175	180
T \bar{G}	2	-6.78	0.52	2.12	-4.15	1.8	85.1	181	-143	-56	186
GG	2	-6.76	0.78	2.46	-3.53	2.5	3 184	179	-101	64	173
G \bar{G}	2	-2.97	0.66	1.99	-0.33	5.7	85.6	169	35	69	164
$\bar{G}\bar{G}$	2	25.50	1.53	4.39	31.42	37.4	3 270	182	32	-72	-229

TABLE IV
 (Continued)

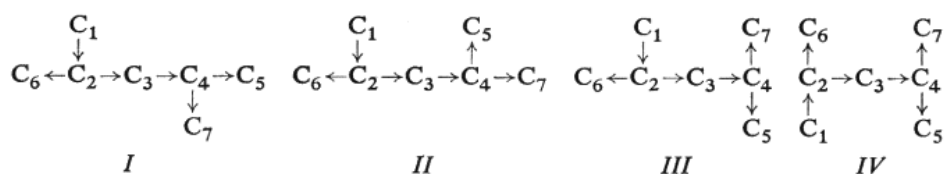
Conformer	<i>k</i>	<i>V_w</i>	<i>V_e</i>	<i>V₃</i>	Total energy		<i>E_{stg}</i>	Dihedral angles			
					abs	rel		C ₁ C ₂	C ₂ C ₃	C ₃ C ₄	C ₄ C ₅
<i>i) (±)-2,4-dicyanopentane</i>											
TT	1	-5.54	2.51	0.33	-2.70	0.7	0.8	180	189	189	180
TG	2	-5.47	1.93	1.62	-1.92	1.5	35.6	190	-68	207	181
T \bar{G}	2	-2.50	7.16	1.51	6.16	9.6	26.6	169	36	190	180
GG	1	-5.50	1.83	0.25	-3.42	0	0	188	-61	-61	188
G \bar{G} a	2	-4.69	2.61	2.31	0.23	3.7	3 184	180	-99	57	174
G \bar{G} b	2	-1.00	1.96	2.80	3.76	7.2	3 184	202	-65	86	161
$\bar{G}\bar{G}$ a	1	12.68	2.40	1.15	16.22	19.6	72.9	167	47	47	168
$\bar{G}\bar{G}$ b	1	7.44	4.76	7.26	19.46	22.9	72.9	125	79	79	125
<i>j) meso-2,4-dicyanopentane</i>											
TT	not present										
TG	2	-5.39	2.03	0.16	-3.20	0	0	187	-65	177	180
T \bar{G}	2	-4.68	2.25	1.79	-0.63	2.6	36.9	172	56	148	180
GG	2	-5.64	1.89	2.42	-1.33	1.9	3 183	179	-101	63	173
G \bar{G} a	2	-4.37	1.96	2.62	0.21	3.4	36.0	179	-104	-66	185
G \bar{G} b	2	-2.90	1.94	1.61	0.65	3.9	36.0	168	41	68	163
$\bar{G}\bar{G}$ a	2	10.63	8.78	3.97	23.38	26.6	3 210	167	41	-78	222
$\bar{G}\bar{G}$ b	2	18.20	9.37	2.02	29.60	32.8	3 210	194	86	-45	178
<i>k) pentane</i>											
TT	1	-4.53	-	0	-4.53	0	0	180	180	180	180
TG	2	-4.44	-	0.17	-4.27	0.3	0.7	180	176	67	175
GG	1	-4.00	-	0.28	-3.72	0.8	1.3	172	61	61	172
G \bar{G}	2	-4.45	-	2.48	-1.97	2.6	3 185	188	-64	101	181

From Table IV*i*, conformer GG is the most stable form of the (\pm) isomer, followed by TT with a relative energy of 0.7 kcal/mol. Experimentally this energy difference has been determined from NMR spectra³ (1.2). However, from NMR spectra, the most stable conformer could not be determined. The sequence of the remaining conformers is similar as in (\pm)-2,4-dichloropentane.

In the *meso*-isomer (Table IV*j*) the conformers form the sequence TG, GG (1.9 kcal/mol), T \bar{G} (2.6), G \bar{G} a (3.4), G \bar{G} b (3.9). Surprisingly no potential energy minimum has been found in the vicinity of the TT form.

TABLE IV
(Continued)

Conformer	k	V_w	V_3	Total energy		E_{stg}	Dihedral angles					
							C_1C_2	C_2C_3	C_3C_4	C_4C_5	C_2C_6	C_4C_7
1) 2,4-dimethylpentane												
<i>I</i>	2	-7.47	0.26	-7.21	0	0	188	-61	179	180	180	188
<i>II</i>	4	-7.74	2.46	-5.28	1.9	3 183	179	-101	64	173	180	180
<i>IIIa</i>	4	-6.79	2.60	-4.20	3.0	3 183	180	-102	-65	186	180	175
<i>IIIb</i>	4	-4.23	3.55	-0.68	6.5	3 183	207	-70	-40	192	180	156
<i>IV</i>	2	15.35	6.18	21.54	28.8	6 368	169	46	-74	224	222	167



k statistical weight of conformer; V_w dispersion energy contribution; V_e dipole-dipole energy contribution; V_3 three-fold rotational barrier contribution; E_{stg} relative energy of conformer in the staggered approximation.

TABLE V
Comparison of Some Theoretical and Experimental Conformer Energy Data in n-Pentane

Conformer	Relative energy			
	calc.	calc. ⁸	calc. ⁹	exp. ²⁵
TT	0	0	0	0
TG	0.26	0.53	0.64	0.50
G^+G^+	0.81	1.18	1.04	?
G^+G^-	2.56	3.20	2.63	?

2,4-Dimethylpentane

2,4-Dimethylpentane differs from all the compounds discussed so far by the absence of polar bonds, and of asymmetric carbon atoms – it does not form stereoisomers. The most stable conformer of this molecule (Table IVe) corresponds by its geometry

to the TT = GG conformer of the syndiotactic diad, or to the TG conformer of the isotactic diad, in agreement with the structure of crystalline polypropylene^{22,23}. The next conformer (relative energy 1.9 kcal/mol) corresponds to the TG form of the syndiotactic diad or to the TT form of the isotactic diad. The presence of a relatively large amount (about 5%) of this conformer could explain the small values of end-to-end distances in isotactic polypropylene²⁴.

Pentane

For comparison, the conformational structure of pentane (Table IVk) regarded as a model of polyethylene, has also been calculated. Pentane has already been investigated by several authors^{8,9,25}. The results of various papers are compared in Table V. Considering the approximations involved in the methods applied, and the differences in the values of dispersion interaction parameters used, the agreement is very good.

CONCLUSIONS

The results obtained by the method described in this paper agree very well with the accessible experimental data. From Table IV, the contributions of all three types of non-bonded interactions of equation (3) are comparable, and it is therefore not possible to neglect any of them in conformer energy calculations. The present calculations confirm recent conclusions based on detailed experimental data, concerning the inadequacy of the "staggered approximation" in studies of conformational structure of larger molecules. In the molecules treated in this paper, not only the relative energies, but also the number and statistical weight of various conformers are found to disagree with expectations based on the "staggered approximation". Most older data on conformer energies in 2,4-disubstituted pentanes which were based on these simplified assumptions will therefore require revision.

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