trans-2-butene and *erythro* yielding 35.4% 1-butene, 34.3% *cis*-2-butene and 30.3% *trans*-2-butene.

Known mixtures of *threo*, *erythro* and ordinary bromides from DBr + 2-butenes were dehydrohalogenated under similar conditions. Synthetic mixture A (9.14 mmoles) containing 85.6% *threo*, 12.8% *erythro* and 1.6% undeuterated 2-bromobutane yielded 5.63 mmoles of purified butenes, 26.6% 1-butene, 12.4% *cis*-2-butene and 61.0% *trans*-2-butene. Mixture B (9.14 mmoles) containing 12.8% *threo*, 85.6% *erythro* and 1.6% ordinary-2-bromobutane yielded 6.0 mmoles of purified butenes, 34.3% 1-butene, 30.3% *cis*-2-butene and 35.4% *trans*-2-butene.

Since method A involved total olefin recovery, it is apparent that a small fractionation error is inherent in method B. These latter results were subjected to a small correction to eliminate the fractionation error.

Rate of Dehydrohalogenation.—A crude determination of the rate of dehydrohalogenation of 2-bromobutane was carried out by dehydrohalogenation of 1.00 ml. (9.14 mmoles) of 2-bromobutane in 50 ml. of 1 *M* potassium ethoxide in absolute ethanol at 70 ± 2°. During the reaction 0.004-ml. samples were taken from the reaction flask and analyzed by vapor phase chromatography with a 10′ Apiezon column at 66° and 60 ml. of helium per minute. The amount of unreacted bromide was determined by its peak area compared to the bromide peak area of a sample taken before the reaction was started. The reaction proceeded as follows: 16 min., 56.5%; 29 min., 69.8%; 45 min., 84.2%; 65 min., 95.6%. The second-order rate constant is $5.0 \times 10^{-2} \pm 0.5$ l. mole^{-1} min.$^{-1}$.

Analysis for Deuterium Content.—Deuterium analysis on the butenes separated by vapor phase chromatography was carried out by determining the amount of undeuterated olefin present in each of the *cis*- and *trans*-2-butene fractions from their infrared optical densities at 14.90 and 10.37 μ, respectively, compared to an optical density *vs.* pressure curve[9] constructed for pure *cis*- and *trans*-2-butenes.

A 35.9-mm. sample of *cis*-2-butene from sample Ib had an optical density at 14.90 μ of 0.222 which corresponds to 23.5 mm. or 65.5% of *cis*-2-butene in the sample. The remaining 34.5% was attributed to 2-deuterio-*cis*-2-butene. A *trans*-2-butene sample, 109.0 mm., from the same bromide had an optical density at 10.37μ of 0.071 which corresponds to 6.25 mm. or 5.7% *trans*-2-butene in the sample. The remaining 94.3% was attributed to 2-deuterio-*trans*-2-butene.

A 65.5-mm. sample of *cis*-2-butene from sample II had an optical density of 14.90 μ of 0.050 which corresponds to 5.0 mm. or 7.6% *cis*-2-butene in the sample. The remaining 92.4% was attributed to 2-deuterio-*cis*-2-butene. A *trans*-2-butene sample, 77.0 mm., from the same bromide had an optical density of 0.679 at 10.37 μ which corresponds to 56.5 mm. or 77.5% *trans*-2-butene in the sample. The remaining 22.5% was attributed to 2-deuterio-*trans*-2-butene.

All spectra were determined in a 5.0-cm. gas cell *vs.* a NaCl plate using a Perkin–Elmer model 21 infrared recording spectrophotometer.

UNIVERSITY PARK, PENNA.
RIVERSIDE, CALIF.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

A Systemized Method of Calculating Dipole Moments and Internuclear Distances in Bicyclic Molecules

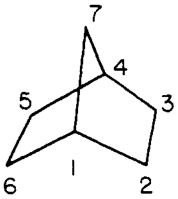
BY C. F. WILCOX, JR.

RECEIVED JUNE 18, 1959

This paper presents tables from which internuclear distances and dipole moments of bicyclo[2,2,1]heptane, bicyclo[2,2,1]-hexane, bicyclo[1,1,1]pentane and their derivatives can be rapidly calculated. Although the models used to derive these tables are highly simplified, calculations and arguments are presented which strongly suggest that more sophisticated treatments would yield essentially identical results.

Introduction

For about fifty years numerous chemists have been interested in the chemistry of molecules which, like bicyclo-[2,2,1]heptane (I) possess strained rings. Recently, several groups of workers have prepared derivatives of the more highly strained bicyclo[2,2,1]hexane (II).[1-3] It appears possible that the still more highly strained bicyclo[1,1,1]-pentane system (III) may also be synthesized.[3]



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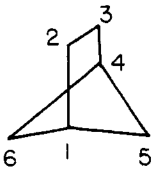

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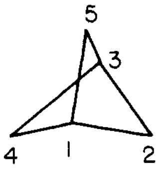

III

The potential availability of derivatives of these three rigid bycyclic systems with the same functional groups offers an opportunity to observe how reaction rates and products change with the varying geometry and strain of the parent system. Among the questions which necessarily will be raised by such future investigations are the essentially geometrical ones of the internuclear separation of two given substituents and the expected dipole moment of some derivative. The purpose of this paper is to anticipate these questions and provide answers in a generalized and systematic form. Tables will be presented from which internuclear distances between any two atoms and dipole moments of simple derivatives of the three hydrocarbons can be calculated rapidly.

Derivation of the Tables.—The formal calculation of internuclear distances and dipole moments is most easily approached by vector methods.[4] The distance between two points (nuclei) is simply the scalar magnitude of the vector joining these points so that this problem reduces itself to a knowledge of the coördinates of the atoms in question. From these coördinates one can immediately write down the vector joining the atoms and, after performing some simple arithmetic, obtain its scalar magnitude (internuclear separation). Similarly, the dipole moment of a molecule is, to the usual ap-

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(1) L. Horner and E. Speitschka, *Ber.*, **88**, 934 (1955).

(2) T. H. Colby, Ph.D. Dissertation, University of Washington, 1957.

(3) J. Meinwald and P. Gassman, page 14-O of Abstracts, 135th Meeting of the American Chemical Society, Boston, Mass., April 6–10, 1959.

(4) For an example of the utility of vector methods see E. J. Corey and R. A. Sneen, THIS JOURNAL, **77**, 2505 (1955).

TABLE I

COÖRDINATES OF BICYCLO[2,2,1]HEPTANE CARBON NUCLEI

		Coördinate	
Atom	x	y	z
1	+1.143	0.000	0.000
2	+0.770	+1.217	− .868
3	−0.770	+1.217	− .868
4	−1.143	0.000	.000
5	−0.770	−1.217	− .868
6	+0.770	−1.217	− .868
7	0.000	0.000	+1.032

TABLE II

COÖRDINATES OF BICYCLO[2,1,1]HEXANE CARBON NUCLEI

		Coördinate	
Atom	x	y	z
1	+1.036	0.000	0.000
2	+0.770	.000	+1.517
3	−0.770	.000	+1.517
4	−1.036	.000	0.000
5	0.000	+1.067	− .399
6	0.000	−1.067	− .399

TABLE III

COÖRDINATES OF BICYCLO[1,1,1]PENTANE CARBON NUCLEI

		Coördinate	
Atom	x	y	z
1	+0.948	0.000	0.000
2	.000	+1.051	− .607
3	− .948	0.000	.000
4	.000	−1.051	− .607
5	.000	0.000	+1.214

proximation, the scalar magnitude of the resultant vector formed by vectorially adding the individual vector bond moments. These vector moments, in turn, are given by the product of the magnitude of the bond moment times the unit vector joining the two atoms. Tables of unit vectors in the directions of all possible substituents would allow ready calculations of dipole moments.

The first set of required quantities are the coördinates of the carbon atoms in the three hydrocarbons. The exact equilibrium values of these coördinates, which correspond to an energy minimum for the molecule, are extremely complicated functions of internuclear distances and bond angles. In order to make the calculations tractable, the following simplifying assumptions have been made: (1) all C–C bonds have a constant length of 1.540 Å.; (2) the strain energy of the molecule can be separated into a skeletal strain energy and an independent external bond strain energy; (3) all internuclear repulsion energies are constant; (4) the bending force constants are the same for all bonds; and (5) the angle strain for a particular bond is given by the quadratic expression $k(\Delta\theta)^2$ where k is the bending constant and $\Delta\theta$ is the deviation in bond angle from 109°28′. The validity of these assumptions will be considered in the Discussion section.

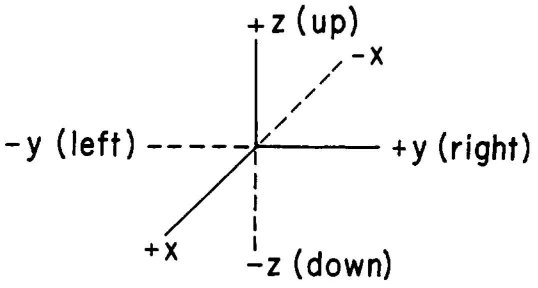

Fig. 1.—Reference coördinate frame.

The first step in obtaining the coördinates was to set up expressions for the skeletal strain energy of the hydrocarbons in terms of characteristic internal angles. The choice is somewhat arbitrary, but for computational convenience the selected angles were: for bicyclo[2,2,1]heptane (I) the angle 123 and the angle between the planes 1654 and 1234; for bicyclo[2,1,1]hexane(II) angle 123 and the angle between the planes 164 and 154; for bicyclo[1,1,1]pentane(III) angle 123. With the given simplifying assumptions all other internal angles are uniquely determined.

The next step was to minimize this internal strain energy and thus obtain the "best" angles.[5] From these angles it is a simple matter to calculate the coördinates. A right-handed Cartesian coördinate frame (Fig. 1) was used with the origin at the midpoint between the bridgehead carbon atoms. The molecules were oriented as in I, II and III, so that the pairs of equivalent wings pointed down. The calculated coördinates for the carbon nuclei of the hydrocarbons are given in Tables I, II and III, respectively. Key skeletal angles are included in Table VII.

The second set of required quantities are the unit vectors which radiate out from the carbon skeleton in the directions of the hydrogens or their substituents. These were obtained for any particular carbon atom by setting up an expression for the external strain energy in terms of the previously calculated local internal angle and a variable external angle followed by minimization as before to give the "best" angle. From these external angles and the previously calculated internal angles and atom coördinates, application of ordinary vector geometry gives the required unit vectors. These vectors, in terms of components along the axes of the coördinate frame defined above, are given for the three hydrocarbons in Tables IV, V and VI, respectively. It has been necessary in these tables to adopt a new nomenclature system in order to indicate the direction of a given unit vector. The reference frame is again a right-handed cartesian coördinate frame and the unit vectors are designated as u (up) or r (right) if they point predominately in the positive y or z direction and as d (down) or l (left) if they point predominately in the negative y or z direction (see Fig. 1).

Sample Calculations.—In order to illustrate the use of the various tables and to demonstrate the simplicity of the method, a dipole moment and an internuclear distance will be calculated. Let us first suppose that one wanted to estimate the dipole moment of 2-*exo*-7-*anti*-dichlorobicyclo[2,2,1]heptane(IV). From the unit vectors of Table IV and the value of 2.1 ± 0.1 D.[6] for the C–Cl bond mo-

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(5) For examples and a discussion of this procedure see: Chapter 12 by F. H. Westheimer in M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956.

(6) This is the measured dipole moment of bornyl and isobornyl chloride; H. Kwart, THIS JOURNAL, **75**, 5942 (1953).

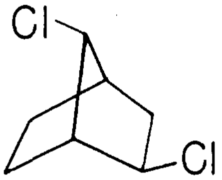
ment, the i, j and k vector contributions of the two C–Cl bonds to the total dipole moment are

$$i\text{-moment} = (2.1)(0.349) + (2.1)(0.000) = 0.733 \text{ D.}$$
$$j\text{-moment} = (2.1)(0.842) - (2.1)(0.824) = 0.038 \text{ D.}$$
$$k\text{-moment} = (2.1)(0.414) + (2.1)(0.566) = 2.058 \text{ D.}$$

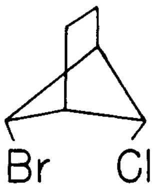
If now the usual assumption is made that the C–H and C–C moments are small and largely cancel in any event, then the total dipole moment of IV is given by equation 1

$$\text{total moment} = [(i\text{-moment})^2 + (j\text{-moment})^2 + (k\text{-moment}^2)]^{1/2} \quad (1)$$

Thus, the calculated moment is 2.19 ± 0.11 D. which compares favorably with the observed[7] value of 2.25 D.



IV



V

As the second example, let us suppose that one wanted to know whether the two halogens of *syn*-5-chloro-6-bromobicyclo[2,1,1]hexane(V) were within van der Waals radii of each other. From Tables II and V and the length 1.7 Å. for the C–Cl bond, the x- y-, and z-coördinates of the Cl atom are

$$x\text{-coördinate} = 0.000 + (1.77)(0.000) = 0.000$$
$$y\text{-coördinate} = 1.067 + (1.77)(0.216) = 1.449$$
$$z\text{-coördinate} = -0.399 - (1.77)(0.976) = -2.127$$

Similarly the coördinates of the Br atom, using 1.91 Å. for the C–Br length, are

$$x\text{-coördinate} = 0.000 + (1.91)(0.000) = 0.000$$
$$y\text{-coördinate} = -1.067 - (1.91)(0.216) = -1.480$$
$$z\text{-coördinate} = -0.399 - (1.91)(0.976) = -2.263$$

From these coördinates of the two halogens the distance between the atoms is calculated by equation 2. The calculated separation is 2.93 Å. which is

$$\text{separation} = [(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2]^{1/2} \quad (2)$$

less than 3.75 Å., the sum of the Cl and Br van der Waals radii, so that *V* would be expected to show effects due to compression of the halogens.

Discussion

In the present calculations of the three hydrocarbon geometries it was expedient to make five simplifying assumptions. The question at hand is whether these assumptions introduce errors which are serious for the limited purpose of estimating dipole moments and internuclear distances. Fortunately, three of the assumptions are easily absolved and will be considered first.

TABLE IV

UNIT VECTORS FOR SUBSTITUENTS OF BICYCLO[2,2,1]HEPTANE

Position	Unit Vector i (x)	j (y)	k (z)
1	+0.927	0.000	+0.376
2u	+ .349	+ .842	+ .414
2d	+ .349	− .115	− .930
3u	− .349	+ .842	+ .411
3d	− .349	− .115	− .930
4	− .927	.000	+ .376
5u	− .349	− .842	+ .411
5d	− .349	+ .115	− .930
6u	+ .349	− .842	+ .411
6d	+ .349	+ .115	− .930
7l	.000	− .824	+ .566
7r	.000	+ .824	+ .566

TABLE V

UNIT VECTORS FOR SUBSTITUENTS OF BICYCLO[2,1,1]HEXANE

Position	Unit vector i (x)	j (y)	k (z)
1	0.928	0.000	−0.373
2l	.360	− .829	+ .428
2r	.360	+ .829	+ .428
3l	− .360	− .829	+ .428
3r	− .360	+ .829	+ .428
4	− .928	.000	− .373
5u	.000	.804	+ .609
5d	.000	.216	− .976
6u	.000	− .804	+ .609
6d	.000	− .216	− .976

TABLE VI

UNIT VECTORS FOR SUBSTITUENTS OF BICYCLO[1,1,1]PENTANE

Position	Unit vector i (x)	j (y)	k (z)
1	+1.000	0.000	0.000
2u	0.000	+ .883	+ .470
2d	0.000	+ .035	− .999
3	−1.000	.000	.000
4u	0.000	− .883	+ .470
4d	.000	− .035	− .999
5r	.000	+ .848	+ .530
5l	.000	− .848	+ .530

From the available data on various cycloalkanes[8] it is clear that C–C bond lengths do not markedly change when the bonds are bent so that the assumption of constant bond length is certainly correct within ±0.03 Å. and is, therefore, acceptable for the present purpose. Similarly, it is possible to show by direct calculations that the "best" external angles are insensitive to changes in the local skeletal angles so that the assumption of separable skeletal and external strain energies is likewise sufficiently valid. Finally, because the bond angle deviations are approximately the same within any one of the hydrocarbons (less than ±8° for I, the worst case), the "best" geometry corresponding to minimum angle strain is rather insensitive to the functional form chosen to represent this strain. This has been dramatically confirmed by the result that when the calculations are repeated using

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[7] H. Kwart and R. K. Miller, THIS JOURNAL, **78**, 5678 (1956).

[8] G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., Appendix and references contained therein.

an alternative assumption that the angle strain is proportional to $\Delta\sigma$ rather than $(\Delta\sigma)^2$ the "best" angles change by only one or two degrees.

The fourth assumption to consider is that of bending force constants which are identical regardless of the substituents on the bonds. This is virtually impossible to evaluate because of the lack of experimental data. It is questionable, even, whether the usual force constants would be appropriate since they contain contributions of non-bonded repulsions which have been treated separately in the present work.[9] A permissive argument which can be applied to discount the seriousness of this assumption is this: stretching force constants, which by their nature are not as susceptible to their surroundings, are known to be quite similar over a large variation in bond type.[10] It might be reasonably inferred that a bending constant which did not include non-bonded repulsions would be analogously independent of at least small variations in bond type.

In contrast to these acceptable assumptions the fifth assumption of constant internuclear repulsion energies might well have been expected to introduce errors which were serious even for the limited purposes of this paper. Examination of Tables I, II and III shows that the assigned separation of the bridgehead carbon atoms are 2.29, 2.07 and 1.90 Å., respectively. The latter two separations are considerably smaller than the diagonal distance of 2.22 Å. in cyclobutane, a molecule which has been described as containing considerable strain and distortion from such internuclear repulsion.[11] There will also be repulsions between pairs of hydrogen atoms and between hydrogen atoms and carbon atoms, It is assumed, however, that these repulsions are, first, much smaller than the carbon–carbon repulsions and, second, the ridigidy of the strained bicyclic systems would prevent alteration of the geometries by twisting.[12]

In order to estimate the magnitude of non-bonded interactions in the three hydrocarbons it is first necessary to select some potential function with which repulsion energy can be calculated as a function of separation. One choice might be the potential function used by Dunitz and Schomaker for their strain energy calculations on cyclobutane.[11] This formula, which is an extension of the Pauling empirical relationship[13] between bond order and internuclear distance, is not a satisfying choice since it requires the broad assumption that a repulsion energy at a given distance can be equated to the energy that a hypothetical bond of this length would possess. It suffers further from the fact that the original Pauling relationship was designed to fit π-bond order rather than σ-bonds. Instead of this function it was decided to use the known repulsion curve for two neon atoms[14] since the van der Waals radius of a neon atom, 1.60 Å.,[15] is quite close to the probable van der Waals radius, 1.57 Å., of a tetrahedrally bonded carbon atom.[16] On the basis of this function and including *only* these non-bonded repulsions, the energies of the three hydrocarbons were minimized. The results were unexpected and quite startling. Although in any one molecule the repulsion energy was of comparable magnitude to the angle strain, the change in skeletal angles was *less than 2°*. These changes are illustrated inTable VII which includes the "best" angles with and without the inclusion of C···C repulsions for certain key angles in the three hydrocarbons. The particular angles obtained by considering non-bonded repulsions results from the balance between a single large bridgehead-bridgehead repulsion and a larger number of smaller repulsions. Increasing the bridgehead separation necessarily forces the bridge atoms closer together. This type of balance suggests that any reasonable function would yield the same result as long as the function had the same general shape as the neon curve. In order to test this suggestion, the calculations were repeated using the Dunitz and Schomaker curve. Although this curve gives repulsion energies which are about twice those obtained from the neon curve (24.7 kcal./mole *vs.* 11.8 kcal./mole at 1.90 Å.), the calculated angles for I are still essentially the same as those derived from the neon curve.

TABLE VII

COMPARISON OF GEOMETRY AS CALCULATED BY ANGLE STRAIN AND BY NON-BONDED REPULSION[a]

Molecule	Angle at one atom bridge	Angle at two atom bridge	Angle between wings
III	76°	. .	120°
	78	. .	120
II	85	100°	139
	85	100	137
I	96	104	109
	94	104	109

[a] The upper angle in each pair is the value calculated on the basis of angle strain. The lower value is calculated on the basis of non-bonded repulsions.

No explanation is offered for this near identity of results obtained by angle-strain and non-bonded repulsion considerations. These results when coupled with the previous discussion do provide, however, a compelling argument that, in spite of the simple model used for the three hydrocarbons, the calculated geometries are close to the truth. It follows, that the tables presented offer a simple procedure for estimating quite good values of internuclear distances and dipole moments of simple derivates of bicyclo[2,2,1]heptane, bicyclo[2,1,1]-hexane and [1,1,1]bicyclo[1,1,1]pentane.

ITHACA, N. Y.

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[9] G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1954, p. 186.

[10] *Ibid.*, p. 142.

[11] J. D. Dunitz and V. Schomaker, *J. Chem. Phys.*, **20**, 1703 (1952).

[12] R. B. Turner, W. R. Meador and R. E. Winkler, THIS JOURNAL, **79**, 4116 (1957).

[13] L. Pauling, *ibid.*, **69**, 542 (1947).

[14] I. Amdur and E. A. Mason, *J. Chem. Phys.*, **23**, 415 (1955).

[15] M. L. Huggins, *Chem. Revs.*, **10**, 427 (1932).

[16] The usual value of the carbon van der Waals radius, 1.85 Å., is based on half thicknesses of aromatic rings and is not applicable here. The value given is obtained from the empirical relationship, r (van der Waals) $= r$ (single bond covalent radius) $+ 0.80$, which can be derived from data given by L. Pauling, "The Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca, N. Y., 1945, pp. 164, 189.