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CONFORMATIONAL ANALYSIS—CIX

APPLICATIONS OF MOLECULAR MECHANICS TO THE STRUCTURES AND ENERGIES OF ALKYNES[1,a]

N. L. ALLINGER* and A. Y. MEYER†
Department of Chemistry, University of Georgia, Athens, GA 30601, U.S.A.

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Abstract—An earlier described force-field has been extended to include alkynes. The structures and heats of formation of simple alkynes were calculated to approximately within experimental error for those for which data are available, and predictions are made for others. Rotational barriers and conformational equilibria were also adequately dealt with. Some macrocyclic alkynes were also examined.

Applications of the method of molecular mechanics to the determination of the structures and energies of organic compounds have become quite extensive during the last few years.[2] Our own studies along these lines have been directed at finding a force field which would be of predictive value for structures and energies, and would be capable of handling all of the common elements and functional groups met with in organic chemistry. Some preliminary studies showed that the method was generally applicable to compounds of a great many different classes,[3] although there were some problems. Our 1973 force field has been previously described, and applied to a sizable number of alkanes,[4] cycloalkanes[4] and alkenes.[5] It has also been applied to carbonyl compounds[6] (aldehydes and ketones) and to silanes.[7] Since the results with the latter two classes of compounds are not very different from preliminary results reported earlier,[8] these calculations need not be further discussed. The method has also been extended to conjugated systems,[9] and to thiols and sulfides.[1] The present paper is concerned with the extension of this same force field to cover acetylenes. This is a class of compounds which does not appear to have been previously studied in any systematic molecular mechanics calculations.

The structural and energy data available on alkynes is rather limited. Structures have been determined by electron diffraction or microwave methods for acetylene itself, and for propyne, 2-butyne, 1-pentyne, 3-methyl-1-butyne, 3,3-dimethyl-1-butyne, as well as for cyclooctyne. Values of stretching and bending force constants are available in the literature.[10] These data enable one to choose the necessary structural parameters, which are assembled in Table 1. Parameters concerning the saturated part of the molecule are carried over from the 1973 force field without change. The van der Waals characteristics of the acetylenic carbon are taken to be identical with those of the vinylic carbon. The C_{sp}–C_{sp^3} bond is assigned a dipole moment of 0·75 D, with a negative end toward the *sp* carbon, and the H–C bond moment is taken to be 0. This fits roughly the dipole moments of simple acetylenes, and provides for the calculation (admittedly crude) of the electrostatic interactions which contribute to the energies of polar molecules. In particular, the computed enthalpy of an acetylene containing two or more C_{sp}–C_{sp^3} bonds (e.g. 2-butyne) includes an electrostatic term, computed by Jeans formula[11] with $\epsilon = 1$.

Table 1. Force field parameters needed for alkynes (van der Waals parameters for Hill equation[5])

Atom	r^* (Å)	ϵ (kcal mole^{-1})
C[a]	1.85	0.030
H[b]	1.50	0.063

Bond stretching parameters

Bond	l_o (Å)	k (mdyn Å^{-2})	Dipole Moment
C≡C	1.212	15.6	0
≡C-C-	1.466	5.2	0.75
≡C-H	1.09	5.9	0

Angle bending parameters

Angle	θ_o	k (mdyne rad^{-2})
-C≡C-H	180	0.24
-C≡C-C-	180	0.38
≡C-C-H	112	0.24
≡C-C-C-	111.5	0.38

Torsional effect

E_{tor} (kcal/mole^{-1}) = 0.53 (1 + cos 3 Φ) for XC–CY where X and Y are any combination of carbon and hydrogen.

Heat of formation parameters (kcal mole^{-1})

	C≡C	≡C-C	≡C-H
normal	+62.294	-1.368	-5.054
strainless[c]	+62.266	-1.961	-5.074

[a] These are the same as for olefinic carbon.

[b] These are the same as for alkane and alkene hydrogen.

[c] Strain is defined as $E + \Sigma H$(bonds) $- \Sigma H$(bonds, "strainless") and parameters are chosen such that acetylene and propyne hav zero strain. The number obtained directly might be calle "inherent strain." To obtain from this number the ordinary strai energy, the excess torsional energy and conformational energy ar added, as appropriate.[2b]

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† On leave from the Department of Organic Chemistry, Hebrew University, Jerusalem.

In order to fit the heats of formation of the alkynes, we must define bond energy parameters for three bonds, C_{sp}–H, C_{sp}–C_{sp^3}, $C_{sp} \equiv C_{sp}$. There are only three possible bonding arrangements about C ≡ C in an alkyne, so one of the three parameters is redundant. We therefore arbitrarily picked the C–H value to have the same numerical constant ($-5{\cdot}054$ kcal mole^{-1}) as was used for a hydrogen attached to either an alkane or alkene carbon. The remaining two parameters were chosen by a least squares fitting to the heats of formation at 25° of six simple alkynes. Results for these six, and for other acetylenes, are shown in Table 2.

Table 2. Heat of formation data for alkynes (kcal mole^{-1})

	ΔH_f^o Exp.[12]	ΔH_f^o Calc.	Error (calc.-exp.)	Strain
Acetylene[a]	54.34 ± 0.19	54.20	-0.14	0.
Propyne[a]	44.39 ± 0.21	43.98	-0.41	0.
1-Butyne[a]	39.49 ± 0.21	39.45	-0.04	0.75
2-Butyne[a]	34.69 ± 0.24	34.57	-0.12	0.81[c]
1-Pentyne[a,b]	34.50	34.32	-0.18	0.90
3-Methyl-1-butyne[a]	32.60	33.20	0.60	1.40
Ethynylcyclohexane[b]		28.45		2.47
1,3-Diethynylcyclohexane				
cis[b]		87.10		4.04
trans		87.34		4.26
3-Methylethynylcyclohexane				
cis[b]		21.28		2.20
trans[b]		21.90		2.82
Cycloheptyne		59.31		31.05
Cyclooctyne		43.43		20.76
Cyclononyne		33.45		16.37
Cyclodecyne		21.39		9.90
1,8-Cyclotetradecadiyne		59.73		5.62

[a] Exp. value used in fitting

[b] Calc. value weighted over various conformers

[c] The computed strain equals the electrostatic contribution to the total energy. If this contribution were ignored, 2-butyne would be strainless by the present force field.

RESULTS

The experimental and calculated structures for simple alkynes are summarized in Table 3. There was no difficulty in fitting the available structures to within experimental error.

The rotational barrier in 1-butyne was calculated to have the value 2·84 kcal/mole (fully relaxed geometries). An experimental value for this barrier does not appear to have been reported, but a value of 3·46 (relaxed geometries) or 3·76 (standard geometries) kcal/mole has been calculated by *ab initio* methods.[21] For 2-butyne, the most recent evaluation of the rotational barrier gave an upper limit of 0·011 kcal/mole.[22] The calculated value we obtain is 0·0 kcal/mole.

1-Pentyne occurs as a mixture of *trans* and *gauche* conformers. It has been concluded that the *gauche* form is of "slightly greater stability", with an energy difference being estimated as 0·077 ± 0·103 kcal/mole.[17] However, the *gauche* conformer is a *dl* mixture, while the *trans* is not, so the *gauche* may be higher in energy, but predominate at equilibrium. The calculations suggest that this is the case. We calculate the enthalpy to be 0·24 kcal/mole greater for the *gauche* conformation, which predicts an equilibrium mixture at 25° containing 57% *gauche* and 43% *trans*.

An interesting feature of 3-methyl-1-butyne is the unusually long C–C bond reported[18] between the secondary sp^3 carbon and the *sp* carbon (1·495 ± 0·011 Å); an analogous lengthening has been reported for 3,3-dimethyl-1-butyne.[23] We calculate a value (1·474 Å) longer than usually found for primary ethynyl derivatives (1·466–1·467), but not as long as the experimental value.

An interesting test of the parameters deduced from the simple acyclic molecules was to apply the calculations to ethynylcyclohexane. It seems safe to assume the ring is in the chair form. Low temperature NMR measurements indicate[24] that the axial form is less stable than the equatorial by 0·41 ± 0·05 kcal/mole. Our calculated value favors the equatorial conformation by 0·50 kcal/mole, in good agreement with experiment. No experimental geometry is available for this compound.

As has been mentioned several times,[2b] the force field of Schleyer gives results which for alkanes are, generally speaking, indistinguishable from those obtained by our force field. The main differences between Schleyer's force field and ours seems to be that he uses a larger carbon atom, and we use a larger H atom. In trying to devise experimental tests that can be used to aid us in improving our respective force fields, ethynylcyclohexane and related compounds come to mind. In particular, we can make predictions regarding *syn*-diaxial groups, in which the pairs involved are methyl-methyl, methyl-ethynyl, and ethynyl-ethynyl. According to our force field, since the H-H interactions are big, and the C–C interactions are

Table 3. Calculated and experimental molecular geometries

Length or angle	Calcd.	Observed[a]	Method and	Ref.
Acetylene				
C≡C	1.212	1.212	ED	14
C-H	1.090	~ 1.09	ED	15
Propyne				
C≡C	1.212	1.206	MW	16
C-C≡	1.467	1.459		
≡C-H	1.090	-		
C-H (Me)	1.095	~ 1.1		
HCH	108.7	108.7		
1-Butyne				
C≡C	1.212			
C-C≡	1.470			
C-C	1.532			
$C^2C^3C^4$	112.0			
C^2C^3H	107.9			
HC^3H	107.7			
2-Butyne (staggered)[b]				
C-C≡	1.468	1.467 ± 0.001	ED	14
C≡C	1.213	1.213 ± 0.001		
C-H	1.095	1.115 ± 0.005		
CCH	110.2	110.7 ± 0.4		
HCH 1	108.8	108.2 ± 0.4		
1-Pentyne (trans)[c]				
C≡C	1.212	1.210	MW	17
≡C-C	1.470	1.460		
≡C-H	1.090	1.060		
≡CCC	111.6	111.5		
≡CCH	108.4	109.5		
3-Methyl-1-butyne				
C≡C	1.212	-		
≡C-C	1.474	1.495 ± 0.011	MW	18
C-C	1.533	1.527 ± 0.003		
≡CCC	110.1	109.6		
CCC	112.2	112.9		
Cycloheptyne[d]				
C≡C	1.213	-	X-ray	19
≡C-C	1.468	1.48-1.50		
C^3C^4	1.550	1.52-1.57		
C^4C^5	1.556	1.47-1.50		
C≡CC	150.4	-		
≡CCC	98.8	110-112		
$C^3C^4C^5$	117.6	119-120		
$C^4C^5C^6$	120.9	122		
HC^3H	110.9			
HC^4H	104.8			
HC^5H	103.4			
Cyclooctyne				
C≡C	1.213	1.232 ± 0.006	ED	20
≡C-C	1.468	1.459 ± 0.012		
C^3C^4	1.544	1.491 ± 0.009		
C^4C^5	1.550	1.584 ± 0.009		
C^5C^6	1.555			
C≡CC	161.5	158.5 ± 0.9		
≡CCC	103.8	110.1 ± 0.7		
$C^3C^4C^5$	115.4	109.6 ± 0.7		
$C^4C^5C^6$	119.1	110.3 ± 0.9		

Table 3 (*Contd*)

Length or angle	Calcd.	Observed[a]	Method	Ref.
HC^{3}H	109.3	108.0 ± 0.5		
HC^{4}H	104.7			
HC^{5}H	102.2			
Cyclononyne[e]				
C≡C	1.214			
≡C–C	1.471			
C–C	1.540–1.546			
CCC[f]	169.7, 109.7, 113.8 115.2, 117.7, 116.0, 114.5, 110.2			
CCCC[g]	2.3, 21.5, 33.4, 81.5, 134.8, 123.2, 77.4, 42.6, 28.2			
Cyclodecyne[h]				
C≡C	1.214			
≡C–C	1.472			
C–C	1.535–1.541			
CCC[f]	1.71.6, 110.3, 116.0, 118.1, 115.4			
CCCC[g]	3.3, 25.6, 69.0, 53.2, 60.6, 169.9			
1,8-Cyclotetradecadiyne[i]				
C≡C	1.213			
≡C–C	1.472			
C–C	1.535 (all)			
CCC[f]	178.3, 111.8, 113.2, 113.9			
CCCC[g]	12,22,64,173			

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[a] Calculated bond lengths should be approximately 0.006 Å longer than experimental MW values.[13]

[b] The same bond length and angles are computed for the eclipsed geometry.

[c] Bond lengths and angles in the C^{2}C^5-gauche structure are very close to those in the trans. Gauche angle 115° (from trans position; exp.[17] 115 ± 3).

[d] The available experimental structure is for a platinum complex.

[e] The computer lowest-energy conformation is asymmetric.

[f] Starting with angle C≡CC and proceeding around.

[g] Starting with dihedral angle CC≡CC and proceeding around.

[h] The computed lowest-energy conformation is of C_2 symmetry.

[i] Only the *trans*-chair, chair conformation was examined. *trans*-Decalin symmetry is conserved in bond angles, and practically so in dihedral angles.

small, we would expect to find that the *syn*-diaxial dimethyl interaction was very large, while the corresponding ethynyl-ethynyl interaction was quite small. We would also expect to find that Schleyer's force field would show the two interactions much more nearly energetically equivalent. While no experimental values are available at this time, appropriate experiments are easily visualized. The predictions of our force field are therefore given for these compounds.

For 1-methyl-3-ethynycyclohexane, *cis* and *trans* isomers are possible. The energies have been calculated for each conformation of each isomer. The energies of the two groups are almost additive, as long as no more than one group is axial. Thus relative energies for the isomers and conformations are as follows: equatorial-equatorial 0·00 kcal/mole; equatorial-methyl, axial-ethynyl, 0·50 kcal/mole; axial-methyl, equatorial ethynyl, 1·57 kcal/mole; axial-methyl, axial-ethnyl, 2·75 kcal/mole. The corresponding diaxial-dimethyl value is 5·17 kcal/mole for reference.

Next, looking at 1,3-diethynylcyclohexane, the following relative calculated energies are obtained: equatorial-equatorial 0·00 kcal/mole, equatorial-axial 0·37 kcal/mole; and axial-axial, 1·22 kcal/mole. Thus we find that, as we had originally supposed, the syn-diaxial methyl interaction is quite big, the syn-diaxial ethynyl interaction is quite a bit smaller, while that for the syn-axial-methyl, ethynyl interaction is intermediate.

When the alkyne linkage is placed into a medium or large ring, one can expect that more or less strain is likely to be introduced. In cycloheptyne, for example, since the acetylene portion of the molecule tends to have four carbons in a line, and the remaining atoms are too few to permit this and give otherwise reasonable bond angles and bond lengths, serious strain is inevitable. As the ring grows larger (cyclooctyne, cyclononyne, cyclodecyne), the problem of angular distortion in the cycloalkyne becomes less acute. The strain does not necessarily become less acute, however, because this depends on other interactions as well. The calculated strain energies obtained are shown in Table 2.

The significance of the strain energies mentioned for the cycloalkynes is perhaps not immediately clear. Perhaps better reference points are the heats of hydrogenation of these alkynes to the corresponding cycloalkanes. Of course, the cycloalkanes themselves are strained to a significant degree. The heat of hydrogenation reflects the difference in strain between the cycloalkyne and the cycloalkane. The calculated heats of hydrogenation for the 7, 8, 9 and 10 membered acetylenes are 87·3, 72·3, 65·4 and 58·8 kcal mole^{-1}; the last three of these heats have been measured in solution and are respectively,[25] >69, 61·9, and 56·6 kcal/mole. It is expected that solvation of the alkynes will lower their heats of hydrogenation in solution, relative to the gas phase.

The lowest-energy conformation for cycloheptyne is calculated to be chair-like, with C^4 and C^6 0·3 Å below, and C^5 0·3 Å above plane $C^3C^1C^2C^7$. Almost of equal energy is a conformation in which all atoms, except C^5, lie in one plane. Another potential minimum corresponds to a twist boat, but this exceeds by 7·4 kcal mole^{-1} the energy of the other two. The cited experimental numbers refer to a complex, $C_7H_{10}Pt(PPh_3)_2$. The seven-membered ring is chair-like, although flatter than the structure we calculate. However, the effect of complexation renders the comparison questionable.

Another piece of information with which our results may be compared is the structure of cyclooctyne, as determined by the electron diffraction method.[20] With such a large molecule, it is difficult, perhaps impossible, to uniquely specify the structure by this method. When our calculated structure is compared with the experimental one, there are some similarities, and some differences. For the similarities, we note that the bond lengths and angles involving the acetylene carbons and the two attached carbons. For the differences, we note that while our calculated structure tends to open bond angles in the aliphatic part of the chain in order to reach around from carbon 3 to carbon 8, the experimental structure has more nearly normal bond angles, but the bond lengths have stretched out considerably. Because of the known ease with which molecules open bond angles, compared to the difficulty of stretching bonds, we feel that our calculated structure is, in this respect, superior to the experimental one. It seems likely to us that a calculated structure based on bond angle opening, rather than on bond stretching, could be determined from the experimental radial distribution curve, and would give an equally good or better fit to the data. The problem here is likely to be simply that the data do not permit a distinction between the two structures, and the interpretation previously put upon the data was not the better of the two possible interpretations.

Cyclononyne is calculated to have a plane of symmetry, and cyclodecyne is calculated to have a C_2 axis of symmetry. Both have moderately well staggered arrangements for the saturated portion of the molecule, and the transannular repulsions are less severe than those found in the corresponding cycloalkanes. The structural data are summarized in Table 3, but no experimental data are available for comparison.

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