Consistent Force Field Calculations. III. Vibrations, Conformations, and Heats of Hydrogenation of Nonconjugated Olefins

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Abstract: A force field for nonconjugated olefins was derived by the CFF method. The set of energy functions included stretching, bending, torsion, twisting, and out-of-plane bending of double bonds, nonbonded atom–atom interactions, and bilinear cross terms. The latter correspond to the valence force field (VFF) type functions and give mostly somewhat better agreement with experiment than the Urey–Bradley (UBFF) functions used previously. The optimized energy parameters comprise 22 parameters for the aliphatic energy functions and 17 for the double bond and its surroundings. Experimental data for the least-squares optimization of energy parameters comprise: 259 experimentally assigned frequencies of ethylene-d_0 and -d_4, *trans*- and *cis*-2-butene, isobutylene-d_0 and -d_8, cyclohexene-d_0 and -d_{10}, 1,4-cyclohexadiene, and *trans,trans,trans*-1,5,9-cyclododecatriene; 44 conformational data on ethylene, propene, *cis*- and *skew*-1-butene, isobutylene, cyclopentene, cyclohexane, *trans*-cyclooctene, *cis,cis*-1,6-cyclodecadiene, 1,5,9-cyclododecatriene, butane, cyclohexane, and cyclodecane; ten cis–trans differences and excess values (over cyclohexene) of heats of hydrogenation involving the 2-butenes, the 1,2-methyl-*tert*-butylethylenes, the 1,2-di-*tert*-butylethylenes, and the five- to ten-membered ring olefins. The inner hydrogens of *cis*-2-butene are found to be eclipsed with the double bond, and relief of strain is obtained by opening the C=C—C bond angles. 1,4-Cyclohexadiene is found to be planar. For *trans*-cyclooctene, the calculated C—C=C—C torsion angle is calculated as 42° off planar. *trans*- and *cis*-cyclononenes are predicted to be similar to the corresponding crystalline *trans*-caprylolactam and its *cis*-hydrochloride, respectively. Less pronounced are the similarities of the cyclodecenes and their silver nitrate adducts. Heats of hydrogenation agree much better with experiments in the gas phase than in acetic acid, where dipolar interactions and other solvent effects interfere.

The calculation of a variety of molecular properties, such as equilibrium conformations, vibrational frequencies, and thermochemical quantities, with the help of a "consistent force field,"[2] has so far been applied to simple saturated hydrocarbons[2] and amides.[3]

In what follows, the evaluation of a consistent force field (CFF) for nonconjugated olefinic hydrocarbons is described.

The study of olefin conformations and thermochemical properties by means of strain-energy calculations has been the subject of previous work.[4] More recently, Favini, Buemi, Zuccarello, and Raimondi[5–7] calculated conformations and energies of cycloalkenes and cycloalkadienes (six- to ten-membered rings). Dunitz[8] discusses the energy requirements for nonplanar deformations of a double bond in his review on conformations of medium rings. It was in fact the corresponding problems pointed out in this latter publication which prompted us to extend the CFF method to the calculation of olefin properties. The strained double bond is the subject of a review by

Zefirov and Sokolov.[9] After the completion of this work, Allinger and Sprague[10] published a paper on the conformations and energies of a series of olefins.

Vibrational spectra of olefins and their normal mode analysis have been the subject of numerous publications. A recent review by Califano[11] covered very satisfactorily all aspects of this subject which are relevant to the present work.

The main feature of the present work, as compared with previous studies on olefins, is that it combines consistently vibrational analysis with conformational and thermodynamic analysis. Consequently, we can calculate the vibrations of strained and unstrained molecules with the same force field while conventional vibrational analysis requires different force constants for strained molecules. The conformational analysis also gains significantly by coupling it to vibrational analysis. Thus the introduction of stretch–bend, stretch–stretch, and bend–bend cross terms, linked with nonbonded interactions, gives better values for all functions involved. Similarly, the inclusion of vibrational enthalpies in the calculated heats of hydrogenation makes the comparison with experiment more realistic.

Potential Functions

In the present work a valence force field combined with nonbonded interactions has been applied. A number of important cross terms have been included. The nonbonded interactions are represented by the 9–6 potential introduced by Warshel and Lifson[2b] for saturated hydrocarbons. Figure 1 gives the defini-

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(7) G. Favini, F. Zuccarello, and G. Buemi, *J. Mol. Struct.*, **3**, 385 (1969); F. Zuccarello, G. Buemi, and G. Favini, *ibid.*, **8**, 459 (1971).

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I Diagonal terms

bond stretch

C $=$ C K_D, b_{OD}

C(sp3)——C(sp3) K_R, b_{OR}

C(sp3)——C(sp2) K_T $=K_R$, b_{OT}

K_I, b_{OI}

K_d, b_{od}

K_r, b_{or} $= b_{od}$

angle bend

H_ϵ, ϵ_0

$H_\sigma \cdot [\sigma_0]$

$H_\omega \cdot \omega_0$

$H_\Lambda = H_\omega \cdot [\Lambda_0]$

$H_\phi \cdot \phi_0$

$H_\psi \cdot [\psi_0]$

$H_\gamma \cdot [\gamma_0]$

$H_\beta = H_\gamma \cdot [\beta_0]$

$H_\eta \cdot [\eta_0]$

$H_\delta \cdot \delta_0$

$H_\alpha = H_\beta \cdot \alpha_0$

torsions

$H_{\Phi E}$

$H_{\Phi O}$

C(sp3)——C(sp2) $H_{\Phi T}$

C(sp3)——C(sp3) $H_{\Phi R}$

out-of-plane bending

H_X

II. Cross-terms

F_{RR}

$F_{R\omega}$

$F_{R\gamma}$

$F'_{R\gamma}$

$F_{\gamma\gamma}$

$F'_{\gamma\gamma}$

$f_{\gamma\omega}$ cos Φ
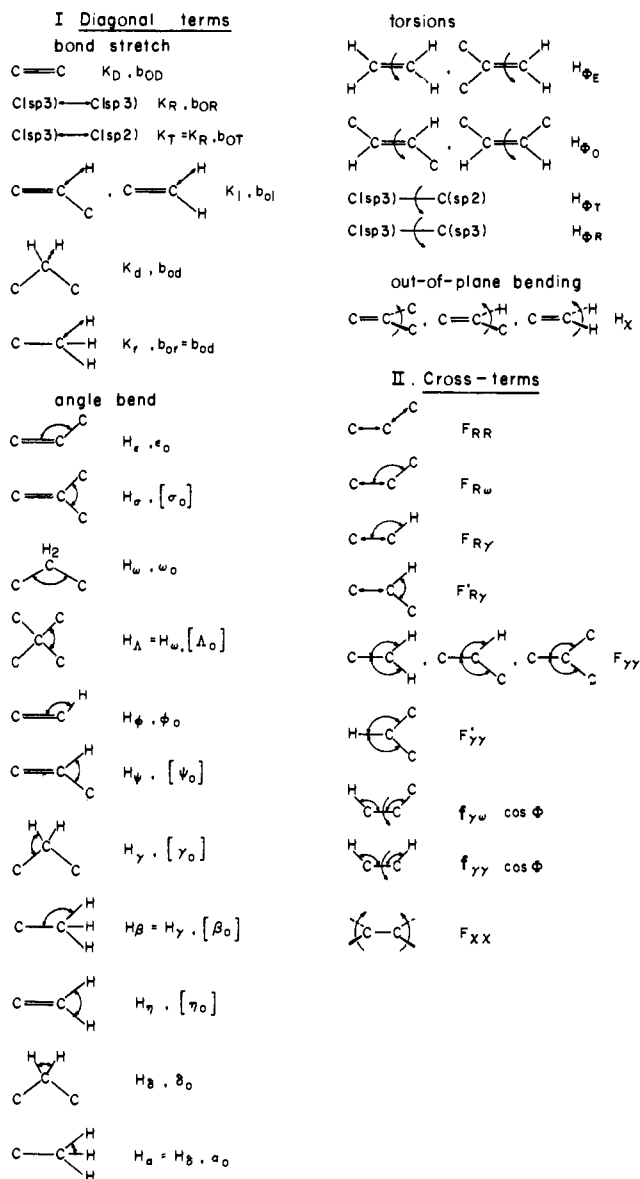
$f_{\gamma\gamma}$ cos Φ

F_{XX}

Figure 1. Definition of the CFF parameters (see section on Potential Functions for further details; dependent reference angles are given in square brackets).

Figure 2. Numbering of the double bond atoms.

tion of the force constants in graphical form. The general expression for the potential is

$$V = \tfrac{1}{2}\sum k_b(b - b_0)^2 + \tfrac{1}{2}\sum H_\theta(\theta - \theta_0)^2 +$$
$$\tfrac{1}{2}\sum H_\chi\chi^2 + \tfrac{1}{2}\sum K_\Phi(1 + s \cos n\Phi) +$$
$$\sum\sum F_{bb}(b - b_0)(b' - b_0') +$$
$$\sum\sum F_{\theta\theta}(\theta - \theta_0)(\theta' - \theta_0') +$$
$$\sum\sum F_{b\theta}(b - b_0)(\theta - \theta_0) +$$
$$\sum\sum F_{xx}\chi\chi' + \sum\epsilon[2(r^*/r)^9 - 3(r^*/r)^6] \quad (1)$$

b, θ, Φ, and χ are the bond lengths, bond angles, torsion angles, and out-of-plane bending angles, respectively; b_0 and θ_0 are parameters representing the corresponding reference values. In the cos $n\Phi$ term, $n = 3$ for all C–C single bonds and $n = 2$ for double bonds. r denotes distances between atoms separated by a chain of three or more bonds. Further explanations are given below.

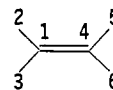Strong correlations exist between some of the reference angles θ_0. For instance, the θ_0 values corre-

sponding to the three angles at the double bond carbon atoms appear correlated if varied independently.[3a] This hampers convergence of the least-squares optimization process. Assuming that in the absence of strain the local symmetries of methylene and methyl groups are C_{2v} and C_{3v}, respectively, and that the double bond carbons are coplanar with their ligands, we introduced the following relations (for notations see Figure 1): cos $\gamma_0 = -$ cos $\tfrac{1}{2}\delta_0$ cos $\tfrac{1}{2}\omega_0$; cos $\beta_0 = -((1 + 2\cos\alpha_0)/3)^{1/2}$; $\eta_0 = 2\pi - 2\phi_0$; $\psi_0 = 2\pi - \phi_0 - \epsilon_0$; $\sigma_0 = 2\pi - 2\epsilon_0$. The number of adaptable parameters has been thus reduced. Λ_0 was given the tetrahedral value of 109.47°. The torsional energy was evaluated individually for each of the torsion angles X–C–C–Y around the C–C bonds, making altogether nine torsional angles for the sp³–sp³ bond and six for the sp³–sp² bond. The torsional energy parameters were $\tfrac{1}{9}$ and $\tfrac{1}{6}$ of the values for $H_{\Phi R}$ and $H_{\Phi T}$ given in Table III, respectively. The values of s in eq 1 are -1 for C=C—C—C and C=C—C—H rotations and $+1$ for all other rotations around single bonds. Out-of-plane deformations of the double bond were taken into account by using two types of functions. For pure twisting around the double bond (i.e., no pyramidal distortion at the sp² carbons) a twofold cos potential was applied, with $s = -1$ and $\Phi = \tfrac{1}{2}(\Phi_{2145} + \Phi_{3146})$ (see Figure 2; Φ_{abcd} denotes a dihedral angle between the two planes defined by the positions of atoms a, b, c and b, c, d, respectively; a sign is attached to this angle, according to the convention recommended by Klyne and Prelog[12]). The definition $\Phi = \tfrac{1}{2}(\Phi_{2146} + \Phi_{3145})$, used by Piaggio, Dellepiane, and Zerbi[13] for the vibrational analysis of trans-3-hexene, is equivalent. For pure out-of-plane bending, i.e., pyramidal distortion without twisting, the potential of Warshel, Levitt, and Lifson[3a] was taken ($\chi = \pi - \Phi_{2143}$, $\chi' = \pi - \Phi_{5146}$; a similar possibility would have been $\chi = \pi - \Phi_{4123}$, $\chi' = \pi - \Phi_{1465}$).

It should be noted that out-of-plane bending is essentially different from torsion, as the first involves the interactions between the three orbitals of the same carbon atom, while the latter involves those between the orbitals of neighboring atoms. Twist and out-of-plane bending are well known to be distinct normal modes in vibrational analysis.

Aliphatic and olefinic carbon and hydrogen atoms were attributed the same nonbonded interactions. Williams has shown[14] that this is a reasonable approximation for crystalline aliphatic and aromatic hydrocarbons.

Cross terms were determined without differentiating between single and double bonds. Vibrational analysis of a number of cyclenes showed that this simplification is permissible. Similarly, the cross terms involving the CH bond were chosen the same for all kinds of CH bonds. Bend–bend cross terms of two angles at

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adjacent carbon atoms were made proportional to cos Φ, as proposed by Warshel and Lifson[2b] (and, similarly, by Brüesch[15]). These authors' assumption, that the constant for HCCC is the geometric mean of the constants for HCCH and CCCC, is not supported, however, by valence force field calculations of alkanes[16] and cycloalkenes.[11] Therefore, we introduced two constants, $f_{\gamma\gamma}$ and $f_{\gamma\omega}$, for HCCH and HCCC, respectively. The cross term corresponding to CCCC was neglected, its influence being in general rather small.[2b,16] The F_{xx} cross term was introduced since it affects strongly the two out-of-plane bending modes of ethylene, though it was found to be less important for cycloalkenes.

Selection of Experimental Data for the Least-Squares Optimization Process

In order to obtain a useful consistent force field, we fit the potential constants to a reasonably large set of data, representing a large variety of structural features. Limiting factors were: availability of reliable experimental data, economy in computing and programming time, as well as the general difficulties of handling simultaneously a multitude of complex calculations. A total of 313 observed quantities was incorporated into the least-squares fitting process: 259 vibrational frequencies, 44 conformational data, and 10 thermochemical quantities.

The vibrational frequencies were selected from the following compounds: ethylene-d_0[17] (12 fundamentals), ethylene-d_4[18] (12), trans- and cis-2-butene[19] (26 each), isobutylene-d_0 and isobutylene-d_8[20] (28 each), cyclohexene-d_0 and cyclohexene-d_{10}[21] (39 and 38, respectively), 1,4-cyclohexadiene[22] (the B_{2u} ring-puckering frequency), trans,trans,trans-1,5,9-cyclododecatriene[23] (49 fundamentals). The experimental frequencies used in the least-squares optimization and the calculated differences obtained are listed in Table I.

The 44 conformational data are listed in Table II. Electron diffraction was the source of data for ethylene,[24] cyclohexene,[25] cis,cis-1,6-cyclodecadiene,[26] n-butane,[27] and cyclohexane.[28] Microwave studies are the source of the data for propene,[29] cis- and skew-1-butene,[30]

and isobutylene.[31] For the ring-puckering angle of cyclopentene the value is derived from the far-infrared spectrum.[32] The conformational data for trans,trans,-trans-1,5,9-cyclododecatriene are the results, averaged over D_3 symmetry, of an X-ray crystal structure analysis.[33] Precise structural information on molecules with nonplanar double bonds is rare. The trans-cyclooctene values (averaged to represent the assumed C_2 symmetry) were taken from an X-ray analysis of the iodine-containing derivative I[34] and hence are of
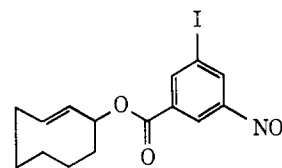
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limited quality. Since one of our main interests for having carried out the present study was in the structure of such molecules we thought it necessary to use these data and tolerated the lack of precision. (The data are torsion angles with an estimated experimental error of 3–4°.) The cyclodecane values represent averages worked out by Dunitz[35] from a number of X-ray analyses of cyclodecane derivatives assuming a conformation with C_{2h} symmetry. The value for the HCH angle is derived from a recent neutron-diffraction study[36] of trans-cyclodecane-1,6-diol (average of four independent values for the HCH angles at the carbon atoms of the same type as 4; see Figure 3). The n-butane[27] and cyclohexane[28] data were included because of their high precision. The conformational cyclodecane properties were introduced into the calculation in order to increase the amount of data from strained systems which are of particular value for the adjustment of the potential constants. Another reason for including the cyclodecane data was that relatively precise HCH angles have not been measured for suitable other compounds.

The enthalpy data are of two kinds, cis–trans enthalpy differences and excess heats of hydrogenation. The difference in the heats of hydrogenation of a cis/trans-olefin pair is given by the cis–trans strain enthalpy difference of the two olefins, assuming that this is the only source of their enthalpy difference. Excess heats of hydrogenation with respect to a suitable reference olefin are given by

$$\Delta\Delta H = H(s) - H(u) - [H_r(s) - H_r(u)]$$

where $H(u)$ and $H(s)$ are the strain enthalpies of the olefin and the corresponding saturated compound, and $H_r(u)$ and $H_r(s)$ are related to the reference compound. Obviously, excess heats of hydrogenation are meaningful only for a class of closely related olefins with similarly substituted double bonds. In the present calculations excess heats of hydrogenation of olefins containing the grouping C—CH=CH—C were

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Table I. Experimental Frequencies and Calculated Differences ($\Delta\nu = \nu_{calcd} - \nu_{obsd}$) Used in the Least-Squares Optimization

Ethylene-d_0 / -d_4

	d_0		d_4	
A_g	3026	−23	2251	−8
	1623	−20	1515	−32
	1342	2	981	−9
A_u	1023	−13	726	−12
B_{1g}	3103	−6	2304	29
	1222	36	1006	8
B_{1u}	949	−32	720	−26
B_{2g}	943	−26	780	−23
B_{2u}	3106	−21	2345	−48
	826	−33	584	−15
B_{3u}	2989	−14	2200	−47
	1444	13	1078	−1

2-Butene (trans- / cis-)

	trans-			cis-	
A_g	3011	40	A_1	3034	13
	2965	15		2979	9
	2926	−43		2931	−43
	1681	7		1669	16
	1455	−11		1462	15
	1389	4		1389	19
	1309	−2		1267	−28
	1145	−18		1009	33
	870	−5		881	−30
	507	−15		304	19
A_u	2960	19	A_2	2979	0
	1471	−25		1462	−23
	1057	−23		1044	1
	964	−6		402	15
B_g	2965	14	B_1	2979	−1
	1455	−9		1462	−19
	1043	2		1016	7
	746	16		685	46
	210	42	B_2	3030	9
B_u	3021	13		2979	−1
	2960	20		1462	−18
	1449	4		1422	−14
	1393	−2		1397	−12
	1311	0		1134	6
	1072	−17		978	−6
	980	24		581	−5

Isobutylene-d_0 / -d_8

	d_0		d_8	
A_1	2980	10	2235	−9
	2941	41	2176	28
	2912	−29	2119	−29
	1661	10	1620	−15
	1470	0	1120	−11
	1416	5	1057	6
	1381	17	1025	5
	1064	−2	856	−11
	807	9	705	19
	387	5	323	7
A_2	971	22	769	−7
	697	18	490	17
	209	−4	148	−2
B_1	3086	3	2309	6
	2972	7	2241	−23
	2893	−10	2086	4
	1458	−4	1267	−33
	1386	10	1053	11
	1282	27	1047	−17
	996	12	797	−14
	974	−29	739	31
	435	−30	367	−30
B_2	2945	35	2204	14
	1444	10	1036	4
	1079	−9	920	−39
	890	32	706	24
	429	−9	363	2
	239	−19	172	−13

Cyclohexadiene-1,4

B_{2u}	108	64

Cyclohexene-d_0 / -d_{10}

	d_0		d_{10}	
A	3026	22	2264	9
	2940	−8	2221	−21
	2916	9	2140	38
	2865	−4	2105	−8
	2839	13	2087	−2
	1656	6	1621	0
	1436	1	1206	−5
	1353	−18	1103	31
	1343	−32	1079	−1
	1241	21	998	−23
	1222	−6	923	−11
	1068	3	899	−16
	966	−12	845	−24
	905	−10	799	−3
	822	27	779	3
	789	24	737	−3
	495	−24	727	−6
	394	3	615	20
	281	11	457	−20
			327	8
			230	9
B	3067	−28	2302	−52
	2960	−32	2206	−18
	2898	28	2182	−3
	2882	−25	2115	−25
	2860	−11	2093	−13
	1450	4	1170	41
	1443	−4	1080	−15
	1392	14	1064	−6
	1338	−10	1048	2
	1321	−27	962	−11
	1265	−4	868	1
	1139	42	791	−1
	1040	24	730	13
	1009	−66	710	15
	917	7	605	−5
	878	−3	497	21
	721	−3	378	18
	643	21		
	455	9		
	175	5		

trans,trans,trans-1,5,9-Cyclododecatriene

A_1	3004	47
	2914	15
	2848	9
	1677	15
	1447	4
	1318	28
	1304	−24
	1208	−8
	1153	−34
	993	−18
	811	6
	482	−9
	331	−11
	174	31
A_2	3032	2
	2919	7
	2844	6
	1430	22
	1350	4
	1302	9
	1169	2
	1041	1
	882	14
	768	21
	266	15
	135	21
E	2934	−5
	2912	14
	2844	13
	2844	6
	1675	14
	1445	9
	1436	15
	1351	−19
	1282	24
	1197	4
	1097	19
	1017	7
	979	3
	955	−7
	914	−6
	855	2
	786	17
	511	1
	488	−19
	375	6
	218	16
	146	−17
	97	4

incorporated. Vibrational, rotational, and translational contributions to the enthalpies were taken into account as described in ref 2a. Cyclohexene was chosen as a reference olefin.

The cis–trans enthalpy difference of the 2-butenes was taken from equilibration measurements[37] in the gas phase at 400°K. That of the 1,2-methyl-*tert*-butylethylenes and the 1,2-di-*tert*-butylethylenes is obtained from heats of hydrogenation in acetic acid solution.[38] Acetic acid solution data also supply the cis–trans energy difference for the cyclooctenes, cyclononenes, and cyclodecenes.[39]

The excess heats of hydrogenation, relative to cyclohexene, of *trans*-2-butene, cyclopentene, cycloheptene, and *cis*-cyclooctene were obtained from heat of hydrogenation measurements of Kistiakowsky and coworkers[40] and refer to the gas phase at 355°K.

Least-Squares Optimization of Force Field Parameters

Initial values for the force field parameters were taken from vibrational spectroscopic investigations[21] and from Herzberg;[41] the optimization of the non-bonded interaction parameters was begun with the values of Warshel and Lifson.[2b]

In the later phases of the optimization process it became evident that some of the potential parameters could be grouped together or omitted. Initially four different parameters H_{Φ_D} for the twist around a double bond were varied individually: one value each for

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Table II. Experimental Values (y_{obsd}), Differences ($\Delta y = y_{calcd} - y_{obsd}$), and Reciprocal Weights ($1/P$) of Conformational and Thermochemical Quantities Used in the Least-Squares Optimization

A. Conformational Properties[a,b]

	y_{obsd}	Δy	$1/P$		y_{obsd}	Δy	$1/P$
Ethylene				**cis,cis-1,6-Cyclodecadiene**			
l_{12}	1.335	-0.002	0.003	l_{12}	1.326	0.007	0.004
l_{23}	1.090	-0.001	0.003	l_{23}	1.506	-0.005	0.006
θ_{123}	121.7	-0.3	0.4	θ_{123}	128.2	-0.1	0.5
Propene				θ_{345}	114.1	-0.7	0.5
l_{12}	1.336	-0.002	0.004	Φ_{1234}	-114.7	-1.1	0.6
l_{23}	1.501	0.003	0.004	Φ_{2345}	58.2	-0.2	0.6
θ_{123}	124.3	-0.4	0.3	**trans,trans,trans-1,5,9-Cyclododecatriene**			
cis-1-Butene				θ_{123}	124.1	-0.6	0.9
θ_{123}	126.7	0.1	0.5	θ_{345}	111.1	0.0	0.9
θ_{234}	114.8	0.0	0.5	Φ_{1234}	178.0	1.6	1.3
skew-1-Butene				Φ_{2345}	-116.5	0.7	1.3
θ_{123}	125.4	-1.4	0.5	Φ_{3456}	63.4	-1.8	1.3
θ_{234}	112.1	-1.0	0.5	**Butane**			
Isobutylene				l_{23}	1.533	-0.002	0.003
θ_{123}	115.3	-0.5	0.3	l_{34}	1.108	-0.002	0.004
Cyclopentene				θ_{123}	112.4	-0.6	0.3
$\Phi_{1534}{}^c$	156.7	1.9	1.0	**Cyclohexane**			
Cyclohexene				l_{12}	1.528	0.005	0.005
Φ_{1234}	-15.2	0.7	1.8	l_{34}	1.104	0.003	0.005
Φ_{2345}	44.9	0.4	1.8	θ_{123}	111.5	-0.5	0.4
Φ_{3456}	-60.2	-1.8	1.8	**Cyclodecane**			
trans-Cyclooctene				θ_{123}	118.0	0.5	0.5
Φ_{8123}	138.0	0.0	2.7	θ_{234}	118.1	0.4	0.5
Φ_{1234}	-88.0	1.0	2.7	θ_{345}	114.7	0.7	0.5
Φ_{2345}	51.0	-0.9	2.7	θ_{748}	105.7	-0.3	0.5
Φ_{3456}	-80.0	-0.7	2.7	Φ_{1234}	66.0	0.1	1.0
Φ_{4567}	112.0	2.8	2.7	Φ_{2345}	55.0	0.0	1.0
				Φ_{3456}	-152.0	1.1	1.0

B. Heats of Hydrogenation, ΔH, kcal mol^{-1}

	Cis/trans differences[d]				Excess values relative to cyclohexene[e]		
	y_{obsd}	Δy	$1/P$		y_{obsd}	Δy	$1/P$
2-Butene	-1.20	-0.05	0.10	trans-2-Butene	0.97	0.0	0.10
1,2-Methyl-tert-butylethylene	-4.29	0.03	1.00				
1,2-Di-tert-butyl-ethylene	-9.37	-2.23	1.00	Cyclopentene	1.68	0.02	0.10
Cyclooctene	9.26	2.02	1.00	Cycloheptene	2.08	0.23	0.10
Cyclononene	2.87	1.91	1.00	cis-Cyclooctene	5.06	-0.23	0.10
Cyclodecene	3.34	-2.46	1.00				

[a] Units: lengths in Å, angles and torsion angles in deg. [b] See Figure 3 for definition of internal coordinates. [c] See Results and Discussion (c) for evaluation of ring-puckering angle. [d] ΔH(cis-olefin) $-$ ΔH(trans-olefin) (note that heats of hydrogenation, ΔH, are negative quantities). [e] ΔH(olefin) $-$ ΔH(cyclohexene).

(a) ethylene, propene, and the 1-butenes; (b) isobutylene; (c) c-C—CH=CH—C; (d) t-C—CH=CH—C. The first two and last two types of constants were finally taken together. Similarly, the same parameters H_χ and $H_{\chi\chi}$ were found to be sufficient for a satisfactory description of all occurring types of out-of-plane bendings. The bend–stretch and bend–bend cross terms $F_{R\gamma}'$ and $F_{\gamma\gamma}'$ were omitted because they refined essentially to zero, and because all the data were insensitive to them.

The choice of an appropriate weighting scheme for the observed quantities in the least-squares calculations presented a problem. Three different kinds of experimental quantities are treated together, and there is no definite rule for establishing their proper relative weights. The weights were chosen proportionally to the inverse "errors" of the data in such a way that the influence of the frequencies, conformational data, and thermochemical quantities on the finally resulting force field parameters were reasonably balanced so as to obtain a consistent predictive power for all three different kinds of properties. The "errors" are understood to comprise not only experimental errors but also the shortcomings of the computational model, for instance the neglect of anharmonicity effects. A reciprocal weight of $1/P$ of 20 cm^{-1} was attached to all frequencies. The reciprocal weights for the conformational data were essentially the reported experimental errors. The enthalpy data valid for the gas phase were given a reciprocal weight of 0.1 kcal mol^{-1}, those measured in acetic acid solution 1.0 kcal mol^{-1}. The final value of the minimized quantity $\Sigma(P\Delta y)^2$ was composed of 75% vibrational, 16% conformational, and 9% enthalpy contributions. An *a posteriori* justification for the relative weights chosen is the fact that the average absolute differences between the calculated and observed quantities are roughly the same as the corresponding reciprocal weights.

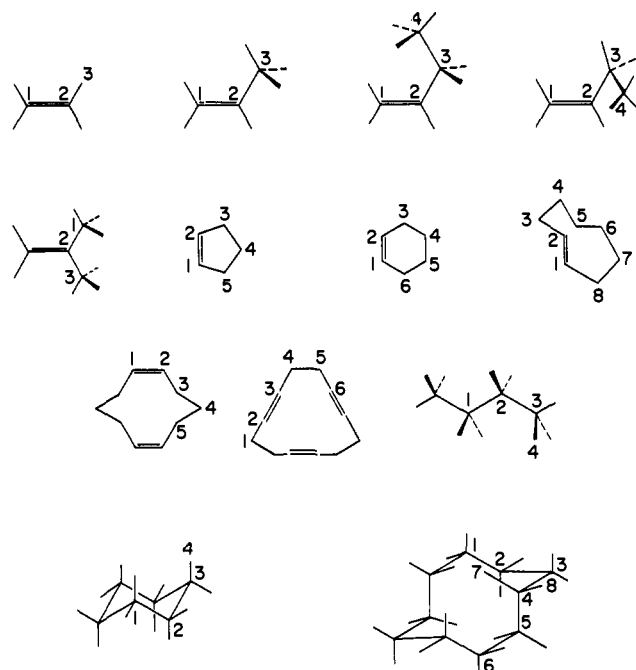The parameter shifts in the iterative least-squares

Figure 3. Atom numbering for notation of the conformational data of Table I.

Table III. Optimized Force Field Parameters[a]

I. Diagonal terms		Torsions	
Bond stretch		H_{Φ_E}	37.9 (1.1)
K_D	1309.9 (18.4)	H_{Φ_D}	32.7 (1.8)
K_R	645.3 (10.9)	H_{Φ_T}	2.532 (0.101)
K_l	723.0 (2.4)	H_{Φ_R}	2.845 (0.122)
K_d	654.0 (2.2)		
K_r	681.5 (2.4)	Out-of-plane bending	
b_{0D}	1.333 (0.002)	H_χ	22.9 (0.5)
b_{0T}	1.501 (0.003)		
b_{0R}	1.526 (0.003)	II. Cross terms	
b_{0l}	1.089 (0.003)	F_{RR}	28.5 (7.3)
b_{0d}	1.105 (0.003)	$F_{R\omega}$	60.2 (6.0)
		$F_{R\gamma}$	38.4 (2.0)
Angle bend		$F_{\gamma\gamma}$	−7.9 (1.1)
H_ϵ	72.4 (4.7)	$f_{\gamma\omega}$	−10.5 (1.4)
H_σ	104.3 (16.4)	$f_{\gamma\gamma}$	−10.0 (0.7)
H_ω	93.2 (5.1)	$F_{\chi\chi}$	3.31 (0.46)
H_ϕ	67.5 (2.1)		
H_ψ	75.0 (3.3)	III. Nonbonded interactions[c]	
H_γ	88.8 (1.1)	$1/2 r^*_{HH}$	1.816 (0.016)
H_η	66.7 (2.2)	$\epsilon^{1/2}_{HH}$	0.0641 (0.0032)
H_δ	79.0 (0.9)	$1/2 r^*_{CC}$	1.759 (0.020)
ϵ_0	122.3 (0.2)[b]	$\epsilon^{1/2}_{CC}$	0.4072 (0.0310)
ω_0	110.5 (0.2)		
ϕ_0	121.2 (0.4)		
δ_0	109.6 (0.5)		
α_0	106.4 (0.6)		

[a] Units: energies in kcal mol^{-1}, lengths in Å, angles in radians, standard deviations in parentheses; see Figure 1 for notation of parameters. [b] See section on Potential Functions for the evaluation of dependent reference angles. [c] The ϵ and r^* parameters, being strongly correlated, were optimized alternatively; therefore, the standard deviation of each parameter was obtained with the other fixed.

process were reduced with the help of a scaling technique.[42] In this method the normal equation matrix A is modified to $A' = A + \lambda E$, with $E_{ij} = A_{ij}\delta_{ij}$; for the present calculations a value of 0.2 for λ was found to yield appropriate parameter shifts. The refinement process was stopped at the point when no parameter shift was bigger than a half of the respective standard deviation. (The average ratio of shift to standard deviation at this stage was 0.12.) A total of 15 refinement cycles was calculated. In the final cycle the value of $\Sigma(P\Delta y)^2$ dropped by 1.0%. The absolute magnitude of all correlation coefficients was less than 0.7 (see Table III).

Results and Discussion

The results of the CFF calculations are summarized in three tables. Tables I and II list all frequencies, conformations, and heats of hydrogenation incorporated into the least-squares fitting procedure. In Table III the optimized CFF parameters, together with their standard deviations, are given. The notation of the conformational quantities is evident from Figure 3. The following discussion consists of four parts: (a) the force field for the olefin calculations, (b) conformations, (c) enthalpies, and (d) vibrational frequencies.

(a) **The Force Field Applied for the Olefin Calculations.** The valence force field (VFF) has been chosen here instead of the Urey–Bradley force field (UBFF) used previously,[2] because the VFF is more general. A VFF can always be modified in such a way as to achieve a better fit between observed and calculated quantities. Disadvantages of the VFF are the computer programming complexities associated with the introduction of new types of cross terms and the time-consuming effort to assess them. A detailed account

on the merits of the two different force fields is given in a recent review by Califano.[11]

The present calculations involve several saturated hydrocarbons, and most of our olefins contain saturated parts; thus the present force field is applicable also to the alkane family.

The charge parameter was omitted from the present calculations after we found that its influence on any of the quantities included in the optimization process was sufficiently small to justify its omission. It seems that many observables, more than previously expected,[2] are insensitive to the charge parameter and the subject is now further examined.[43]

Our consistent force field is similar in many respects to the VFF used by Califano,[11] and a comparison of the two is of some interest (Table IV). Nonbonded interactions are included only in the CFF, and some parameters are quite different; e.g., the CCC bending constants H_ϵ and H_ω are lower in the CFF, while the bending constants involving hydrogens are rather similar. A correlation between nonbonded interactions and bending constants was considered qualitatively by various authors[44,45] who introduced reduced angle bending constants in strain calculations.

(b) **Conformations.** The average absolute differences between the 44 observed and calculated bond lengths, bond angles, and torsion angles used in the optimization of parameters are 0.003 Å, 0.5°, and 1.0°, respectively.

(42) D. W. Marquardt; J. Soc. Ind. Appl. Math., **11**, 431 (1963); R. Fletcher, U. K. Atomic Energy Authority, Theoretical Physics Division, Harwell, Berkshire, 1971.

(43) A. Hagler, private communication.

(44) J. E. Williams, P. J. Stang, and P. v. R. Schleyer, Annu. Rev. Phys. Chem., **19**, 531 (1968).

(45) N. L. Allinger, M. T. Tribble, M. A. Miller, and D. H. Wertz, J. Amer. Chem. Soc., **93**, 1637 (1971).

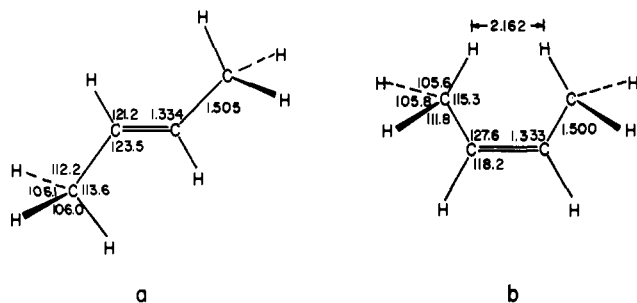Figure 4. Calculated geometries of (a) trans- and (b) cis-2-butene (symmetries C_{2h} and C_{2v}, respectively).

Table IV. Comparison of Some of the Optimized CFF Parameters (Table III) with Spectroscopic Force Constants Derived by Califano, et al., for Cyclohexene[21] (A) and trans,trans,trans-1,5,9-Cyclododecatriene[28] (B)

	CFF	A	B
K_D	1309.9	1252.8	1253.1
K_R	645.3	631.3	631.3
K_l	723.0	729.8	712.4
K_d	654.0	655.5	651.5
H_ϵ	72.4	132.0	131.0
H_ω	93.2	151.3	151.1
H_ϕ	67.5	72.6	72.0
H_ψ	75.0	68.7	69.1
H_γ	88.8	95.2	95.6
H_δ	79.0	78.3	77.8
H_{Φ_D}	32.7	32.0	47.2
H_{Φ_T}	2.532	1.92	2.02
H_{Φ_R}	2.845	2.30	2.30
H_χ	22.9	23.9	21.5
F_{RR}	28.5	16.0	15.6
$F_{R\omega}$	60.2	60.9	60.3
$F_{R\gamma}$	38.4	49.9	49.6
$F_{\gamma\gamma}$	-7.9	-4.6	-4.3

In the following, some conformational details are discussed.

1. 2-Butenes. trans-2-Butene poses no conformational problems. The conformation and some calculated geometry parameters of the C_{2h}-symmetric molecule are given in Figure 4a. The agreement with electron diffraction (ED) results[46] is satisfactory.

The cis isomer is structurally more interesting. If it would have the same geometry as propene, where the inner methyl hydrogen is coplanar with the double bond, the distance between the inner hydrogens would be only 1.80 Å. Thus the question arises whether the repulsion between these hydrogens will open the bond angles to allow a minimum energy conformation of strict C_{2v} symmetry or whether a lower symmetric C_2 conformation with twisted methyl groups and/or a nonplanar double bond might be more favorable. Allinger and Sprague[10] suggested a twisted C_2 conformation. The experimental evidence of ED[46] on this question was not conclusive but from a recent microwave (MW) analysis[47] C_{2v} symmetry was definitely deduced. Our Newton–Raphson minimization technique yielded a C_{2v} conformation as a true minimum, even when the minimization was started with a severely distorted (twisted methyl groups, nonplanar double

(46) A. Almenningen, I. M. Anfinsen, and A. Haaland, Acta Chem. Scand., 24, 43 (1970).
(47) S. Kondo, Y. Sakurai, E. Hirota, and Y. Morino, J. Mol. Spectrosc., 34, 231 (1970).
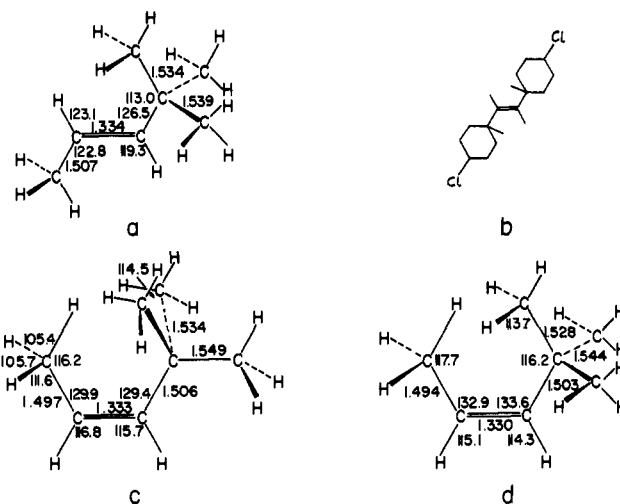
Figure 5. Calculated geometries of the 1,2-methyl-tert-butylethylenes: (a) trans isomer, symmetry C_s; (b) compound with known crystal structure, containing carbon skeleton of cis isomer; (c) cis isomer, symmetry C_s; (d) cis isomer, symmetry C_s, alternative conformation.

bond) C_2 model. From Figure 4b it is seen that the above-mentioned H$\cdots$H interaction causes an opening of the C—C=C and the inner H—C—C angles (127.6 and 115.3°, respectively). The MW value of the C—C=C angle is 126.7° and that of ED is 125.4°. Indeed, twisting of the double bond or the methyl groups in cis-2-butene is not an effective mechanism of increasing the short inner H$\cdots$H distance since the hydrogens are moved perpendicular to the line connecting them. Angle opening moves the two hydrogens essentially along the connecting line and is therefore more effective. In other words, a relatively small adjustment of angles has the same effect as comparatively large changes of torsion angles, so that angle bending may be preferred to torsional deformations despite the higher force constants involved.

The methyl groups are calculated to possess an only slightly distorted local C_{3v} symmetry and to be tilted outward by 2.3°, while an inward tilt of 0.9° and an outward tilt of about 5° were obtained by MW and ED, respectively. The short H$\cdots$H contact is calculated to be 2.162 Å. The increased energy of cis-2-butene as compared with the trans isomer is mainly due to the higher angle strain of the former (cis–trans difference of this type of strain is 1.10 kcal mol^{-1}). The nonbonded energy of the cis isomer is only 0.21 kcal mol^{-1} above that of trans-2-butene.

2. 1,2-Methyl-tert-butylethylenes. Their structures have not been studied experimentally. For the trans isomer the conformation of Figure 5a (C_s symmetry) is probably the most favorable one. The fact that 1-butene consists of a conformational mixture containing an appreciable amount of the syn planar conformer[30] supports this assumption.

For the cis isomer one might draw conformational conclusions from an X-ray analysis[48] of the compound shown schematically in Figure 5b, which contains the structural unit of interest in this context. The X-ray coordinates of this compound, which has a twisted double bond, provided the starting model for cis-1,2-methyl-tert-butylethylene. The resulting geom-
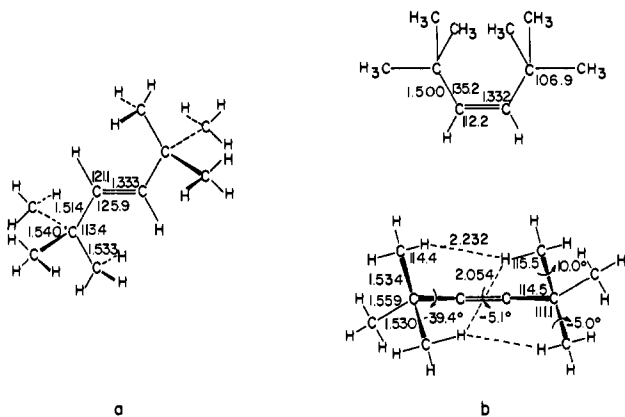
(48) D. Mootz, Acta Crystallogr., Sect. B, 24, 839 (1968).

Figure 6. Calculated geometries of the 1,2-di-*tert*-butylethylenes: (a) trans isomer, symmetry C_{2h}; (b) cis isomer, symmetry C_2. Rotations of the *tert*-butyl groups are measured from the eclipsed position with respect to the double bond; rotations of the methyl groups are measured from the staggered position with respect to the =C—C single bond.

Figure 7. Calculated geometries of cyclopentene and 1,4-cyclohexadiene.

etry is shown in Figure 5c. The conformation has C_s symmetry and hence a planar double bond. An energetically unfavorable feature of this conformation is the staggered arrangement of the double bond with respect to the *tert*-butyl group which results in a torsional strain of 2.6 kcal mol^{-1}. As an alternative a second conformation with C_s symmetry was examined with the double bond eclipsed with respect to the *tert*-butyl group. The corresponding geometry of minimum energy is given in Figure 5d. The removal of torsional strain is compensated mainly by an increase (2.8 kcal mol^{-1}) of angle strain. Including vibrational contributions, the enthalpy of the conformation of Figure 5d is higher than that of the other conformer by 0.8 kcal mol^{-1}.

3. **1,2-Di-*tert*-butylethylenes.** No experimental structure determination is available. The conformation of the trans isomer is most likely as in Figure 6a (symmetry C_{2h}). The conformation of the cis isomer was assumed to be similar to the analogous partial conformations in 2,3-di-*tert*-butylquinoxaline (DTBQ), 4,5-di-*tert*-butylimidazole (DTBI), and 1,2,4,5-tetra-*tert*-butylbenzene (TTBB), three compounds for which X-ray analyses have been published recently.[49] Geometric details of the minimum energy conformations (C_2 symmetry) are given in Figure 6b. The most striking effect of the repulsions between the nonbonded *tert*-butyl hydrogens is the calculated opening of the C—C=C angles by 12.9° relative to the reference value of 122.3°. The double bond deviates only slightly from planarity (C—C=C—C torsion angle = 5.1°); this is similar to the X-ray results of the three abovementioned compounds.[49] This small double bond deformation does not primarily increase the short H···H distances but rather allows the *tert*-butyl groups to rotate somewhat further away from their unfavorable staggered orientation with respect to the double bond. Our calculations do not, therefore, support Mock[50] who considers a relief of steric compression in cis-1,2-di-*tert*-butylethylene by torsion around the

double bond. According to our CFF, this relief is achieved almost entirely by bond angle opening.

The calculated bond lengths appear normal. Wiebenga and Bouwhuis[51] calculated a double bond length of 1.356 Å and a C(sp^2)–C(sp^3) length of 1.557 Å with the help of a simple scheme devised for evaluating the strain energy and geometrical features of overcrowded compounds containing *cis-tert*-butyl groups. The application of this scheme, which critically rests on the experimental geometries of DTBQ, DTBI, and TTBB, to cis-1,2-*tert*-butylethylene does not seem completely legitimate. Opening of the C—C=C angles in the latter compound is probably energetically cheaper than in the three aromatic compounds: in the olefin the *tert*-butyl groups are not attached to rigid rings and there is no equivalent to the *o*-hydrogens or the nitrogen lone pairs of the aromatics, which likewise disfavor angle opening as a mechanism for reducing the nonbonded repulsions. The CFF energy minimization of 1,2-di-*tert*-butylcyclohexene, which is more closely related to the aromatics discussed above, yields stretched C=C and C(sp^2)–C(sp^3) bonds: 1.352 and 1.530 Å (1.536 Å within the six ring), respectively. Our calculated bond stretchings have, however, to be judged with caution, since no geometry data of molecules with abnormal bond lengths were involved in the determination of the CFF parameters.

A further effect of the H···H repulsions is noted in Figure 6b; the four inner methyl groups are rotated slightly out of ideally staggered partial conformations in such a way as to make more room for the inner hydrogens. Finally, it is interesting to mention that the highest calculated methyl CH-stretching frequency of the cis isomer (corresponding to a symmetric mode which involves the movement of the two hydrogens separated by 2.054 Å; see Figure 6b) exceeds the corresponding frequency of the trans isomer by 29 cm^{-1} (3011 and 2982 cm^{-1}, respectively).

4. **Cyclopentene.** The conformation of cyclopentene is mirror symmetric with the symmetry plane bisecting perpendicularly the double bond. Hence, the C—C=C—C torsion angle is zero and the ring puckering angle can be expressed in terms of the improper torsion angle Φ_{1534} (Figure 7a; puckering angle = $\pi - \Phi_{1534}$). The ring-puckering angle was introduced into the least-squares optimization process and a value of 21.4° was calculated. From far infrared, microwave, and electron diffraction experiments puckering angles of 23.3 ± 1, 22.3 ± 2, and 29.0 ± 2.5°

(49) DTBQ: G. J. Visser and A. Vos, *Acta Crystallogr., Sect. B*, 27, 1793 (1971); DTBI: G. J. Visser and A. Vos, *ibid.*, 27, 1802 (1971); TTBB: C. H. Stam, *ibid.*, 28, 2715 (1972).
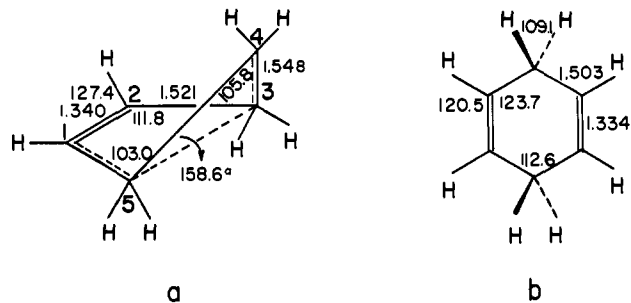(50) W. L. Mock, *Tetrahedron Lett.*, 475 (1972).

(51) E. H. Wiebenga and E. Bouwhuis, *Tetrahedron*, 25, 453 (1969).

were derived, respectively.[32,52,53] The energy difference between the planar and the puckered conformations was deduced from far ir analysis[32] to be 0.66 kcal mol^{-1}. Our calculated value for this barrier is 0.36 kcal mol^{-1}; Allinger and Sprague[10] obtained 0.41 kcal mol^{-1}.

5. 1,4-Cyclohexadiene. Earlier experimental evidence,[54] as well as a recent far-infrared study,[55] leaves little doubt that 1,4-cyclohexadiene has a planar D_{2h} structure, a result which is borne out by our calculations. (For geometrical details see Figure 7b; the minimization was started with a nonplanar C_{2v} structure in which the dihedral angle between the double bond planes was 120°.) Oberhammer and Bauer[56] interpreted results of electron diffraction experiments in terms of a nonplanar C_{2v} structure with the planes of the two double bonds forming an angle of 159.3°. Dallinga and Toneman,[57] on the other hand, analyzed their electron diffraction results as strongly favoring the planar D_{2h} model. As supporting evidence for the C_{2v} structure, Oberhammer and Bauer refer to the nonplanarity of 9,10-dihydroanthracene derived from an X-ray crystal structure analysis[58] and quote a semiempirical strain calculation of Herbstein[4b] which also yielded a nonplanar structure. The conformation of 1,4-cyclohexadiene is mainly determined by two factors. Angle strain favors a nonplanar six-ring, since the sum of the four C—C=C and the two C—C—C reference angles is 9.8° smaller than 720° (Table III). Torsional strain on the other hand favors planarity. The net result is a planar structure since the C=C—C—C torsion angles vary so much faster with small ring puckering than the CCC angles that angle bending is less effective despite the relatively high force constants involved. The situation is reversed in 9,10-dihydroanthracene because the torsional barrier around a C–C single bond attached to a benzene ring is distinctly smaller than the torsional barrier around a C–C single bond adjacent to an olefinic double bond,[59] so that here angle strain becomes the dominant factor. Conformational comparisons between olefins and their benzo derivatives have to take into account this important difference with regard to torsional barriers. Herbstein's calculations on 1,4-cyclohexadiene are not conclusive as far as the planarity problem is concerned, since he did not consider the influence of torsional strain.

6. Cycloheptene. The conformational properties of cycloheptene have been studied experimentally by vibrational spectroscopy[60] and by nmr techniques.[61] Observed spectra were in both cases interpreted in terms of a C_s symmetric chair form as the most stable conformation. Detailed experimental structure determinations have not been published. Three conformational types were considered in our calculations

Figure 8. Calculated cycloheptene geometries (a–c) and experimental geometry of ε-caprolactam (d) (peripheral values: bond lengths and angles; others: torsion angles): (a) chair, symmetry C_s; (b) C_2 form; (c) twist-boat, no symmetry.

(Figure 8). The mirror symmetric chair of Figure 8a is the most stable conformation in agreement with previous calculations,[5,10] although the C_2 form of Figure 8b has an enthalpy calculated to be only 0.42 kcal mol^{-1} higher (vibrational contributions taken into account; this holds for all following stability comparisons). The conformation of Figure 8c is a very distorted boat (no symmetry) and is less stable than the chair by 2.64 kcal mol^{-1}. The C_s-symmetric boat has four unfavorable torsion angles and corresponds to an energy maximum in our calculations. Thus we confirm Allinger and Sprague's[10] result that the C_2 twist form is only slightly above the chair form but not their proposal that the boat is another local minimum. In Figure 8d the geometry of ε-caprolactam as obtained from a crystal structure analysis[62] is given for comparison. This compound possesses a slightly distorted chair conformation. The pattern of bond angles and torsion angles resembles quite closely that of the calculated chair conformation of cycloheptene, in particular if one excludes the double bond and amide moieties from the comparisons which make up the difference between the two compounds.

7. Cyclooctenes. There is good experimental evidence as to the type of conformation of cis-cyclooctene,[63] though its detailed structure has not yet been determined. It can be derived from the chair-boat conformation of cyclooctane by placing the double bond at the position of the smallest torsion angle. In Figure 9a details of the calculated conformation (no symmetry) are given. For comparison, the similar geometrical results of an X-ray study of enantholactam hydrochloride[64] are shown in Figure 9b. It should

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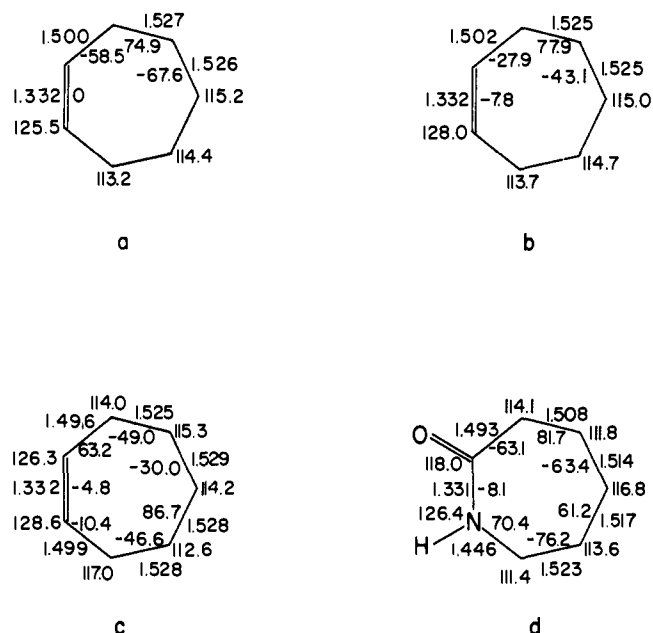(62) I. Nitta, M. Haisa, N. Yasuoka, K. Kasami, Y. Tomiie, and Y. Okaya, Annu. Rep. Fiber Res. Inst. Osaka Univ., No. 17, 1 (1965).
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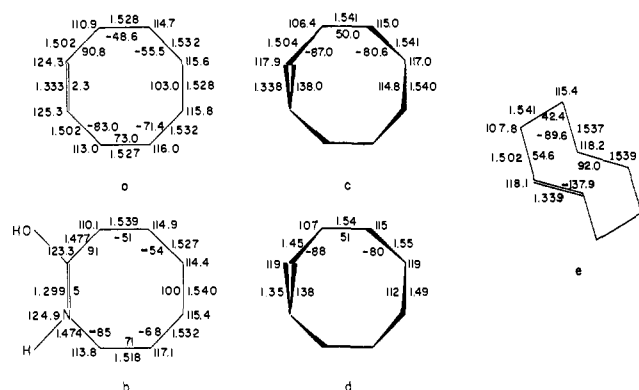(64) F. K. Winkler and J. D. Dunitz, J. Mol. Biol., 59, 169 (1971).

Figure 9. Cyclooctene geometries (peripheral values: bond lengths and angles; others: torsion angles): (a) cis-cyclooctene calculated, no symmetry; (b) enantholactam hydrochloride observed; (c) trans-cyclooctene calculated, symmetry C_2; (d) trans-cyclooctene as observed in an iodine derivative (C_2 averages); (e) trans-cyclooctene calculated, distorted chair conformation, symmetry C_2.
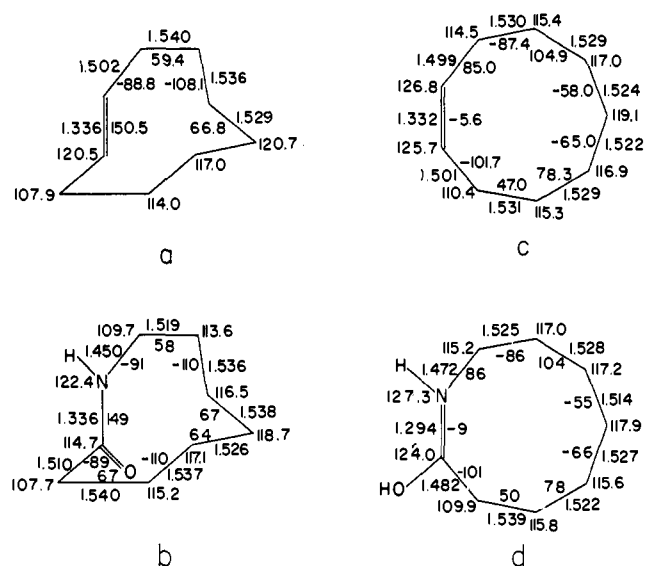

Figure 10. Calculated cyclononene geometries and observed geometries of caprylolactam (b) and its hydrochloride (d) (peripheral values: lengths and angles; others: torsion angles): (a) trans-cyclononene, symmetry C_2; (c) cis-cyclononene, no symmetry.

be mentioned that the minimization was started with a model possessing torsion angles different from the corresponding ones of the minimum conformation by up to 20°; the derivatives of the energy with respect to the cartesians after minimization were less than 10^{-7} kcal mol^{-1} Å^{-1}. Previous authors[5,10] also concluded that the conformational type of Figure 9a is the most favorable for cis-cyclooctene.

The conformations of three derivatives of trans-cyclooctene have been analyzed by X-ray techniques, two with metal-complexed double bonds[65] and one noncomplexed iodine-containing derivative.[34] All three ring conformations are similar and show approximate C_2 symmetry (Figures 9c and 9d). The torsion angles of the eight-membered ring of the iodine derivative were used as data in the optimization process (Table II). The agreement between the calculated and observed, highly nonplanar, C—C=C—C torsion angle is particularly satisfactory. The energy required for the nonplanar distortion of the double bond is nearly equally distributed between twisting and out-of-plane bending (3.75 and 3.44 kcal mol^{-1}, respectively). Favini, et al.,[6] favor a C_2 symmetric distorted chair form for trans-cyclooctene. A conformation of that type was minimized with our force field (Figure 9e). Its enthalpy is 3.14 kcal mol^{-1} higher than that of Figure 9c.[65a] Favini's calculations yield a C—C=C—C torsion angle of −163.0°, while our value is −137.9°. Allinger and Sprague[10] are qualitatively in accord with our results.

8. Cyclononenes. No detailed conformational properties of the cyclononenes are known. We derived the conformational models for trans- and cis-cyclononene from two recent crystal structure analyses of caprylolactam and its hydrochloride.[64] Figure 10 gives a comparison of the minimized two cyclononone conformations and the corresponding observed geometries of caprylolactam and caprylolactam hydrochlo-

ride. It is again striking how similar the conformational details of the olefins and the corresponding lactams are. In particular, the conformations of cis-cyclononene and caprylolactam hydrochloride are very closely related. This is not surprising in view of the enhancement of the double bond character of the C(O)—N bond on protonation of the amide oxygen. The experimental enthalpy of trans-cyclononene is 2.9 kcal mol^{-1} higher than that of the cis isomer. The corresponding trans–cis difference in the free lactams would be smaller due to the lower double bond character of the amide group. The protonated lactams would have a larger difference, i.e., more similar to the olefins, because of the enhanced double bond character. This reasoning offers an explanation why the protonated lactam crystallizes in the cis conformation, while the free lactam yields more readily to other forces in the crystal which appear to prefer the trans conformation. Favini and coworkers[6] assumed local mirror symmetry in the olefinic and local C_2 symmetry in the aliphatic halves of cis-cyclononene. Our results (Figure 10c) show significant deviations from these local symmetries, but the conformational types are qualitatively similar.

9. Cyclodecenes. The crystal structures of the silver nitrate adducts of cis- and trans-cyclodecene have been studied by X-ray analysis.[66,67] A derivative of the trans isomer (trans-cyclodecen-5-yl p-nitrobenzoate) with a noncomplexed double bond was also investigated.[68] It was found that the 10-ring conformations in the crystals of the two trans-cyclodecene derivatives are of different types. We analyzed seven different trans-cyclodecene conformations, and six of them were within 2.5 kcal mol^{-1}. The conformation presented in Figure 11a (C_2 symmetry) possesses the lowest minimum enthalpy and corresponds to the X-ray result of the AgNO$_3$ complex (Figure 11b). The

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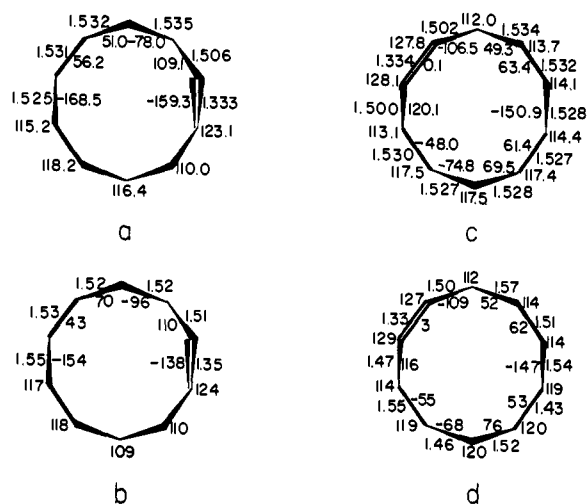(68) O. Ermer, Ph.D. Thesis, ETH Zurich (No. 4465), 1970; J. D. Dunitz, Pure Appl. Chem., 25, 495 (1972).

Figure 11. Cyclodecene geometries (peripheral values: lengths and angles; others: torsion angles). *trans*-Cyclodecene: (a) calculated, symmetry C_2; (b) observed (AgNO$_3$ complex, C_2 averages). *cis*-Cyclodecene: (c) calculated, no symmetry; (d) observed (AgNO$_3$ complex).
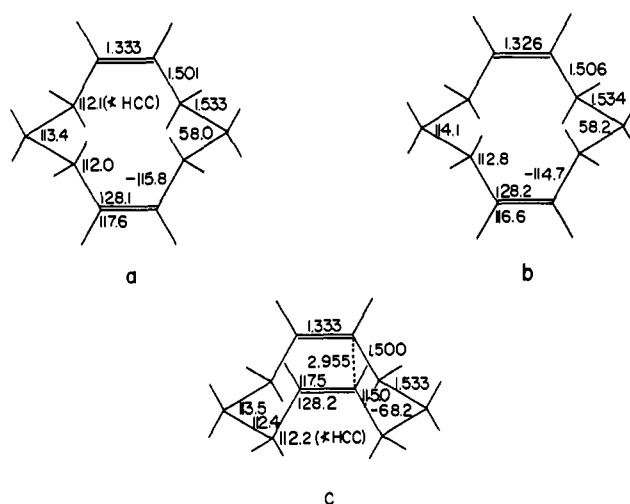
Figure 12. Geometries of *cis,cis*-1,6-cyclodecadiene (lower right values: torsion angles; others: bond lengths and angles). C_{2h} conformation: (a) calculated; (b) observed; (c) C_{2v} conformation calculated.

conformation of the *p*-nitrobenzoate crystals was calculated to be less stable by 2.02 kcal mol^{-1}. Further details will be dealt with in a future publication.

For *cis*-cyclodecene two conformations were minimized, one of them (Figure 11c) corresponding to the AgNO$_3$ adduct[36] (Figure 11d); the other proved to be 1.92 kcal mol^{-1} higher.

A comparison of the *trans*- and *cis*-AgNO$_3$ adducts with the corresponding calculated conformations (Figure 11) reveals strikingly larger differences for the trans than for the cis isomer. The molecular packing arrangements in the crystals of the AgNO$_3$ adducts of the cyclodecenes are very similar.[66,67] It is therefore unlikely that crystal forces are primarily responsible for the rather large discrepancies. Apparently the silver coordination plays an important role. Neutron diffraction investigations of a metal complex containing a platinum-coordinated ethylene molecule (Zeise's salt)[69] show that the ethylene ligand is nonplanar and adopts C_{2v} symmetry; *i.e.*, the cis torsion angles remain zero, while the trans torsion angles deviate from 180°. Silver coordination of a double bond should have a qualitatively similar effect. For a cis double bond close to planarity only a small coordination effect on the C—C=C—C torsion angle is expected, while for a trans double bond the absolute value of this angle should be reduced. For *trans*-cyclodecene the upper limit of this reduction is estimated as 21° (Figures 11a and 11b; a comparison of these two figures reveals considerable differences for other ring torsion angles as well; furthermore, one of the calculated CCC angles exceeds the corresponding observed value in the AgNO$_3$ complex by 7°). It was thought that the influence of the silver coordination could be understood in terms of a perturbation of H_χ, H_{Φ_D}, and H_{Φ_T}. However, an attempt to vary these CFF parameters systematically by least squares (taking the C_2-averaged observed angles and torsion angles of the complex conformation as data) in such a way as to reproduce the ten-ring con-

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formation of the AgNO$_3$ complex failed: H_χ and H_{Φ_T} were adjusted to unreasonably small values without consistent conformational changes of the ten ring. The problem requires a more detailed study.

The calculated conformation of *cis*-cyclodecene agrees reasonably well with that observed for the AgNO$_3$ adduct and is very closely related to the stable cyclodecane conformation.[66] The largest difference belongs to a ring segment which is characterized by high thermal motion in the crystals of the adduct and therefore by poorly defined atomic positions.

The trans and cis conformations calculated by Favini, *et al.*,[6] are all different from our most favorable conformations. Our results agree with those of Allinger and Sprague[10] on the favorable conformation of *cis*-cyclodecene. However, their suggested C_2 twist form as the favorable trans conformation seems to have synclinal torsion angles on both sides of the double bond, while our C_2 twist has these torsions as 109° (Figure 11a). Thus, the conformations appear to be different.

10. *cis,cis*-1,6-Cyclodecadiene. Available experimental[26,70] and computational[71] evidence on the conformation of *cis,cis*-1,6-cyclodecadiene leads to a C_{2h}-symmetric chair conformation. Some results of an electron diffraction analysis[26] were used as data for the force field optimization (Table II). In Figures 12a and 12b calculated and observed geometrical details are given for comparison. Another possible conformation with C_{2v} symmetry is shown in Figure 12c. Its calculated enthalpy is higher by only 0.16 kcal mol^{-1} than that of the C_{2h}-symmetric conformation. From this one would have predicted the occurrence of a conformational mixture consisting of roughly equal amounts of the C_{2h} and C_{2v} forms. According to electron diffraction,[26] the molecule exists predominantly in the C_{2h} conformation and possibly to a minor extent in the C_{2v} conformation. Thus our cal-

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culated enthalpy difference seems to be too small. The reason might be that the *parallel* double bonds in the C_{2v} form repel each other more than calculated with our functions for the nonbonded interactions, due to orbital symmetry considerations.

(c) Enthalpies. The average absolute difference for the ten heats of hydrogenation is 0.92 kcal mol^{-1}. It is low (0.11) for the gas data and rather high (1.73) for the solution data.

The heats of hydrogenation of a number of mono-olefins have been measured both in acetic acid solution and in the gas phase[38,72] and differences of up to 1.7 kcal mol^{-1} were found, which are apparently due to solution effects.[73] Therefore, in the least-squares process considerably lower weights were given for the solution data as compared with the gas data (Table II). Four out of five of our calculated values do not agree satisfactorily with the solution data. In the case of the cyclooctenes, for instance, the calculated cis-trans difference turns out to be higher (by 2.0 kcal mol^{-1}) than the observed value. *trans*-Cyclooctene has a rather high dipole moment[74] (0.8 D) and should be relatively better stabilized by the polar solvent (acetic acid) than *cis*-cyclooctene (dipole moment 0.4 D). In cyclodecene, the situation is reversed, namely the dipole moment of the cis isomer is larger than that of the trans isomer, in line with the calculated cis-trans difference being smaller than the experimental one (by 2.5 kcal mol^{-1}). A similar reasoning may hold also for the 1,2-di-*tert*-butylethylenes. It is more difficult to estimate such an effect for the cyclononenes, whose dipole moment difference is unknown. Other solution effects may also play a role. For instance, *trans*- and *cis*-1,2-methyl-*tert*-butylethylene have probably different dipole moments, but their calculated value for the cis-trans difference fits experiment well. Measurements of enthalpies of solution could help to clarify the solvent effect. Alternatively, gas-phase equilibration studies would be welcome.

The calculations of the heats of hydrogenation depend, of course, on the correct conformational choices for the individual olefins and the corresponding saturated hydrocarbons. For simplicity we chose in all cases the conformations of calculated lowest enthalpy and did not allow for conformational mixing when encountered.

The calculated and observed heats of hydrogenation of the cyclenes with five- to ten-membered rings are compared in Table V. The following conformational assumptions were made for the cyclanes involved in the calculation of these heats of hydrogenation. The cycloheptane skew-chair was preferred to the skew-boat (both of C_2 symmetry) being more stable by 3.86 kcal mol^{-1}. The stable conformation of cyclooctane was assumed to be the chair-boat form (C_s symmetry). The conformational analysis of cyclononane poses a problem. In the crystals of cyclononylamine hydrobromide[75] the nine-ring possesses an approximate C_2 symmetry. On the other hand, a recent nmr study by Anet and Wagner[76] strongly supports a D_3-sym-

Table V. Calculated[a,b] and Observed[c] Heats of Hydrogenation, ΔH, of the Five- to Ten-Membered Cyclenes

	$-\Delta H_{calcd}$	$-\Delta H_{obsd}$
Cyclopentene	26.85 (−0.69)	26.92
Cyclohexene		28.59
Cycloheptene	26.26 (0.34)	26.52
cis-Cyclooctene	23.74 (0.29)	23.53
trans-Cyclooctene	35.01 (0.34)	32.24
cis-Cyclononene	22.61 (0.34)	23.62
trans-Cyclononene	27.39 (0.51)	26.49
cis-Cyclodecene	19.37 (0.26)	20.67
trans-Cyclodecene	20.22 (0.35)	24.01

[a] Calculations for the gas phase at 298°K; reference olefin: cyclohexene; vibrational contributions are given in parentheses. [b] See Results and Discussion (b and c) for conformational assumptions. [c] Cyclopentene through *cis*-cyclooctene: measurements in the gas phase at 355°K; *trans*-cyclooctene through *trans*-cyclodecene: in acetic acid at 298°K.

metric structure. Previous conformational calculations[77,78] favored the D_3 form by 3-4 kcal mol^{-1}. Our present CFF calculations favor the above-mentioned C_2 conformation by 0.31 kcal mol^{-1}. We chose this C_2 conformation for the present calculations of the heats of hydrogenation.

(d) Vibrational Frequencies. Our CFF analysis of vibrational spectra comprises seven different molecules plus three perdeuterated species, providing a total of 259 frequencies. This is the largest number of olefins hitherto analyzed simultaneously. This large scope has helped to remove some ambiguities unresolvable in the study of single molecules.

The average absolute difference between observed and calculated values of the 259 frequencies used in the optimization process is 15.4 cm^{-1}, the maximum absolute difference 66 cm^{-1}.

The torsional vibrations of the methyl groups in *cis*- and *trans*-2-butene are a good example of the interrelation between vibrational and conformational analysis, characteristic of the CFF method. The repulsion between the inner hydrogens in *cis*-butene must reduce the methyl torsional frequencies, as compared with those of the trans isomer. Our calculated frequencies are 179 cm^{-1} (B$_1$) and 132 cm^{-1} (A$_2$) for the cis isomer and 252 cm^{-1} (B$_g$) and 195 cm^{-1} (A$_u$) for the trans isomer. Experimental infrared and Raman experiments for these very weak modes are difficult. Richards and Nielsen[79] assigned the frequencies 290 and 210 cm^{-1} to the two cis torsions and the two trans torsions, respectively, contrary to the above consideration. However, a very recent far-infrared and laser Raman study of methyl-substituted ethylenes[80] is in close support of our considerations and results.

A more detailed discussion of the normal mode assignments of some of the olefins included in Table I, as well as the calculated frequencies and a number of new assignments of 1,4-cyclohexadiene and of cyclopentene, will be presented elsewhere.

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