

ON THE RELEASE OF STRAIN IN OVERCROWDED SUBSTITUTED ETHYLENES

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Abstract—Minimum energy conformations of all possible Me, i-Pr, and t-Bu substituted ethylenes as well as some mixed methyl-t-butyl substituted ethylenes have been calculated using a consistent force field derived by least-squares fitting of a large set of observed conformational, vibrational, and thermochemical olefin properties. Large angle deformations and nonplanar double bond distortions were obtained for t-Bu containing systems. Nonbonded interactions appeared to decrease Me torsional frequencies of *cis*-dimethyl substituted ethylenes and to increase Me C-H stretching frequencies of *cis*-di-t-Bu substituted ethylenes.

INTRODUCTION

In a recent study¹ of conformational, vibrational, and thermodynamic properties of alkene molecules by the consistent force field (CFF) method,² we considered several cases of conformational change due to overcrowding around the C=C double bond. In *cis*-2-butene, for example, the two inner Me hydrogens and the double bond are eclipsed, as in propene. However, if the various bond angles of *cis*-2-butene would remain the same as in propene, the inner H...H distance would be only 1.8 Å and the resulting repulsion would force the inner hydrogens apart. This separation may be effected either by widening the C=C-C and inner H-C-C angles, or by nonplanar distortions of the double bond, or by rotating the Me groups. Which is preferable? The Me rotation has a soft potential but moves the inner hydrogens perpendicular to their line of separation, thus small rotations do not release the strain. Nonplanar double bond deformations are geometrically of a similar character and involve a harder potential. Bond angle widening also has a comparatively hard potential but moves the inner hydrogens away from each other along their line of separation. Our calculations, confirmed by experiment,³ showed that strain is released in this case by angle bending alone.

We also studied¹ the conformational and strain-energy differences between the *cis*- and *trans*-isomers of some bulkier substituted ethylenes (1,2-methyl-t-butylethylene and 1,2-di-t-butylethylene), where overcrowding is much more pronounced. In the di-t-butyl case, for example, the calculated *cis*-*trans* strain energy difference is 11.6 kcal/mole (Experimental 9.4) and the conformational response

to the strain is comprised of large angle bendings and torsions around the C-C single bonds adjacent to the double bond.

Here we wish to present a more systematic study of the substitution of the hydrogens of ethylene by bulky groups. When is angle bending the only response to overcrowding? When do the bulky groups rotate around the single bonds adjacent to the double bond, and when do out-of-plane deformations of the double bond occur? Can a systematic pattern be recognized in the ways by which the strain around the double bond is released, and in the ways by which strain energy is accumulated? It is impossible to answer such questions by qualitative considerations only, so we sought the answers by calculating with our CFF the equilibrium conformations and strain energies of a representative set of substituted ethylenes. The set included all possible methyl, i-propyl, and t-Bu substituted ethylenes. Also included in the set were some ethyl and mixed methyl-t-butyl substituted ethylenes.

The applicability of our CFF¹ to substituted ethylenes has been satisfactorily established. However, some of our calculated conformations reported here are extremely overcrowded and the internal coordinates deviate so much from their reference values, that one should expect the predictions regarding extreme cases to be inexact. For example, calculated C=C-C bond angles widen up to 137°. Quadratic energy terms for such wide angles may not be satisfactory, so the calculated equilibrium coordinates may be in some error. However, the picture which emerges from the calculations with regard to the set of molecules as a whole is correct, we believe, in its general outlines, and may serve as a guide for further experimental work in this field.

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RESULTS AND DISCUSSIONS

The conformations, as derived by our calculations, are presented schematically in Figs 1-4. For many of these molecules the energy of several conformations was minimized. With the exception of 1-butene, only those of lowest energy are given here. We tried to include in the figures most internal coordinates of interest, but had to omit the rest of them in order to avoid numerical overcrowding. More detailed lists of minimum energy Cartesian and internal coordinates, strain energy contributions, and vibrational frequencies may be obtained on request.

For quantitative comparison of energies, the strain energies ΔE_{str} are listed in the Table. The values are given in the last column and are calculated from the preceding columns. The equilibrium energy V_{eq} is obtained (Ref 2) as the minimum value of the energy V , where V is the sum of all CFF functions for bond stretching, angle bending, torsions, out-of-plane bending of the double bond, and nonbonded interactions. The vibrational contribution to the energy E_{vib} is obtained by the standard statistical mechanical formula using the calculated fundamental modes of vibration as obtained from the matrix of second derivatives of V_{eq} . It is calculated for room temperature (298°K). E_{int} is the sum of V_{eq} and E_{vib} . Only differences of E_{int} have a physical meaning, since V_{eq} does not include the heat of formation, and its reference value is arbitrary. Let ΔE (methyl) be the difference between E_{int} (propene) and E_{int} (ethylene). It represents the increase of E_{int} by substituting a hydrogen atom by a methyl group in ethylene. Substituting 2, 3 or 4 ethylenic hydrogens by Me groups should involve 2, 3 or 4 times ΔE (methyl) respectively, if not for the strain energy accompanying this process. Therefore the strain

energy ΔE_{str} of any Me substituted ethylene may be calculated by $\Delta E_{str} = E_{int} - E_{int}(\text{ethylene}) - n \cdot \Delta E$ (methyl) where n is the number of Me substituents. Similarly we define $\Delta E(i\text{-Pr})$ and $\Delta E(i\text{-Bu})$ from which we may calculate the strain energies of *i*-Pr and *i*-Bu substituted ethylenes. The reader will verify from the Table that $\Delta E(\text{Me})$, $\Delta E(i\text{-Pr})$, and

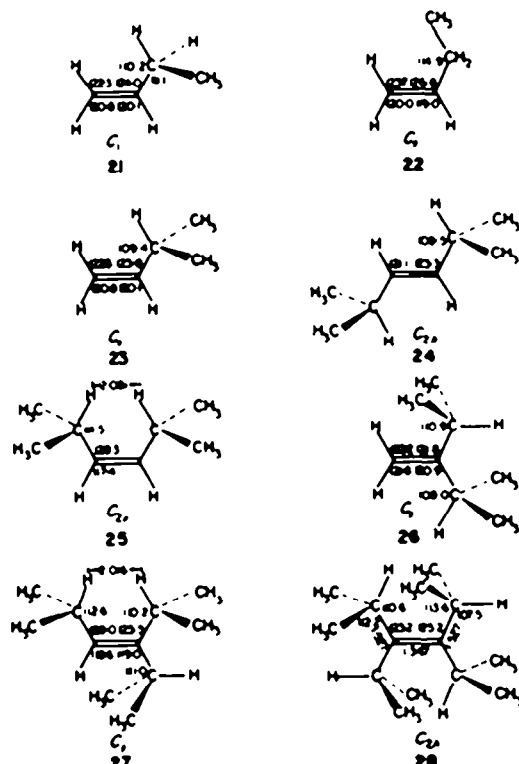


Fig. 2. Butene-1 and *i*-propyl substituted ethylenes.

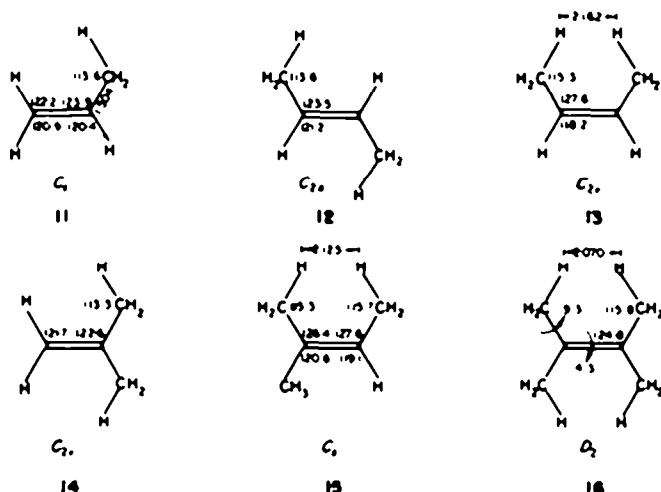


Fig. 1. Methyl substituted ethylenes.

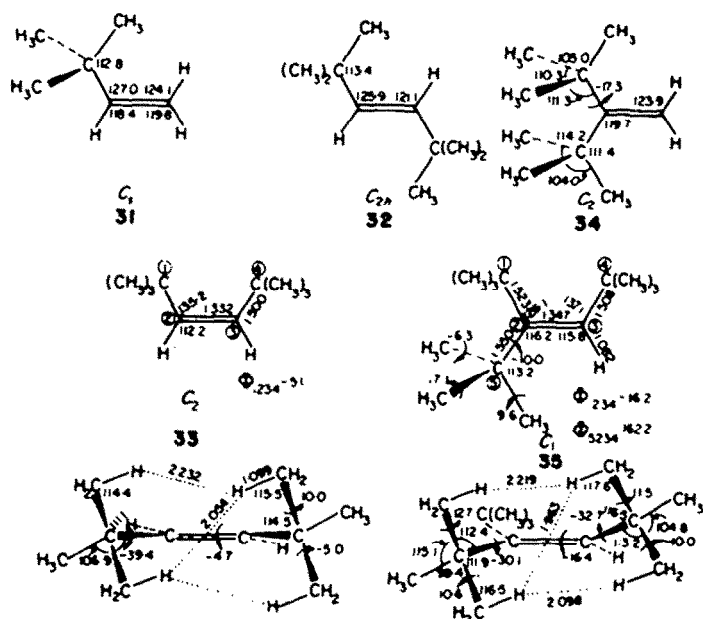


Fig 3. *t*-Butyl substituted ethylenes. Rotations of the *t*-butyl groups are measured from the eclipsed position with respect to the double bond; rotations of the methyl groups are measured from the staggered position with respect to the $\text{C}-\text{C}$ single bond. Φ_{me} denotes a dihedral angle between the two planes defined by the positions of atoms a, b, c and b, c, d, respectively (atom numbers encircled). The rotation angles around the double bonds are those of pure twisting as defined in Ref 1.

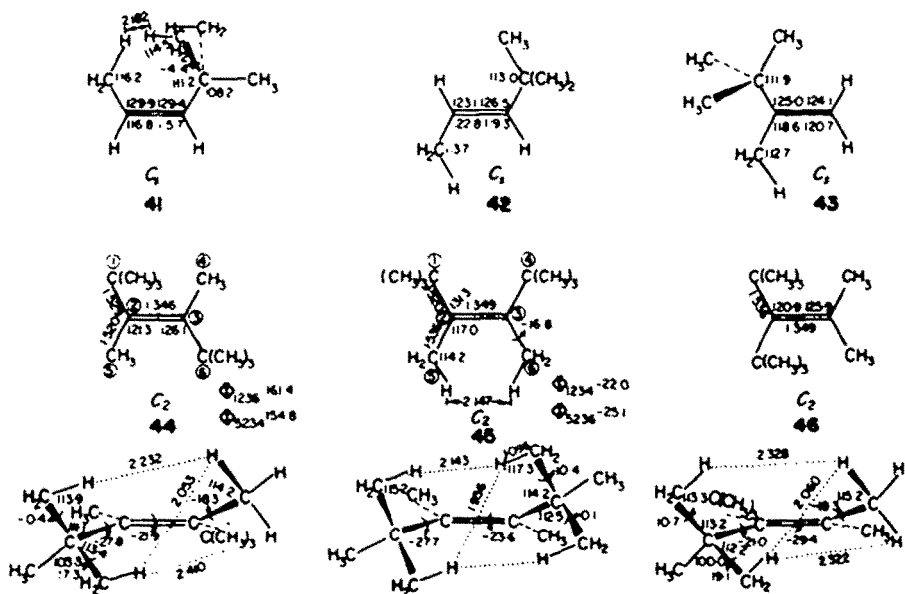


Fig 4. Some mixed methyl and *t*-butyl substituted ethylenes. The explanations of Fig 3 are valid for this figure as well.

$\Delta E(\text{t-Bu})$ are 18.85, 56.09 and 76.92 kcal/mole respectively, and that ΔE_{me} is readily derived from E_{me} using these values.

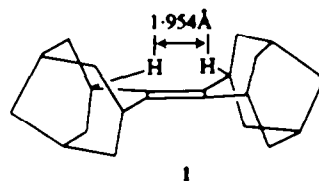
Many interesting conclusions may be drawn from a detailed inspection of Figs 1-4 and the Table. We

shall point out here only a few of the more general ones.

Among the Me substituted ethylenes, tetramethylethylene has the shortest inner H...H distances and the highest strain energy, and is the

Table. Strain energies (kcal/mole) of substituted ethylenes; the numbering of the molecules corresponds to the figures

	V_{∞}	E_{∞}	E_{int}	ΔE_{int}
Ethylene	0.29	32.59	32.88	—
11	0.83	50.90	51.73	0
12	1.26	69.09	70.35	-0.23
13	2.41	69.20	71.61	1.03
14	1.59	68.98	70.57	-0.01
15	3.36	87.00	90.36	0.93
16	6.81	105.50	112.31	4.03
21	1.50	69.06	70.56	0
22	2.47	69.15	71.62	1.06
23	2.22	86.75	88.97	0
24	3.63	141.56	145.19	0.13
25	5.03	141.71	146.74	1.68
26	7.11	141.54	148.65	3.59
27	10.28	196.23	206.51	5.36
28	23.50	251.59	275.09	17.85
31	4.75	105.05	109.80	0
32	8.65	177.60	186.25	-0.47
33	19.97	177.85	197.82	11.10
34	20.10	178.67	198.77	12.05
35	43.57	252.15	295.72	32.08
41	5.05	123.33	128.38	-0.27
42	9.30	123.32	132.62	3.97
43	6.99	123.49	130.48	1.83
44	29.93	214.84	243.87	19.45
45	35.69	215.31	251.00	26.58
46	39.55	215.53	255.08	30.66



only one for which angle bending alone cannot release the strain optimally, so it must resort to C-C torsional and C=C twisting deformations. However, these deformations are small (9.3° and 4.3° , respectively). The energy of the D_{2h} -symmetric conformation with eclipsed Me groups and a planar double bond is only 0.18 kcal/mole higher than that of the twisted D_2 -symmetric conformation. It forms, therefore, a rather low barrier for flipping from one D_2 -conformation to its mirror-image. Adamantylideneadamantane (1) contains the skeleton of tetramethylethylene but is calculated to have a D_{2h} -symmetric structure with a planar double bond and eclipsed inner hydrogens the nonbonded distance of which is only 1.954 Å. The main reason for this difference compared to tetramethylethylene is the blocked torsions around the C(sp²)-C(sp³) single bonds in adamantylideneadamantane. The minimization of tetramethylethylene with a corresponding barrier artificially increased by 30% already yields a D_{2h} -structure as a true minimum. An X-ray analysis of adamantylideneadamantane crystals⁷ showed no significant deviations from molecular D_{2h} symmetry, in agreement with our gas phase calculations.

All the most favourable conformations of *i*-propyl substituted ethylenes (Fig 2) are calculated

to contain planar double bonds. The tertiary hydrogen atoms in *cis*-1,2-di-*i*-propylethylene are eclipsed as in *cis*-2-butene, and the strain is low. In 1,1-di-*i*-propylethylene one tertiary H atom is synplanar and the other antiplanar with respect to the double bond, and due to geminal *i*-propyl interactions the strain energy is quite high. In tri-*i*-propylethylene the above arrangements are superimposed and the strain energy is seen to be the sum of those of 1,1-di-*i*-propylethylene and *cis*-1,2-di-*i*-propylethylene.

Four out of the six *t*-butyl ethylenes (Fig 3) involve torsional strain. The tri- and tetra-substituted compounds have nonplanar double bonds. The double bond of *cis*-1,2-di-*t*-butylethylene is almost planar.¹ The geminal nonbonded repulsions are considerably larger than in the *i*-propyl substituted ethylenes (Table). The strain of 1,1-di-*t*-butylethylene is similar to that of *cis*-1,2-di-*t*-butylethylene which itself is a highly strained compound. The strain distribution is, however, quite different. The 1,1-isomer is strained mainly due to nonbonded interactions while for the 1,2-isomer angle bending contributes prominently to the strain. An energy minimization of tetra-*t*-butylethylene was performed although the result for this extremely strained system can be only qualitatively meaningful considering our simple cosine potential for the double bond twist with a relatively low barrier (37.9 kcal/mole) derived essentially from vibrational frequencies. The results of this calculation are therefore not represented in Fig 4 and the Table. It can nevertheless be concluded that this compound must contain a very highly twisted double bond (calculated 75°). The calculated energy V_{∞} is very high (86 kcal/mole). The synthesis of this molecule is being attempted.⁶ 2,3-di-*t*-butyl-*trans*-2-butene (Fig 4) has a double bond calculated to be twisted by 22° . For comparison we note that in the crystals of 2,3-bis-(*cis*-4-chloro-1-methyl-cyclohexyl)-*trans*-2-butene, a molecule which contains the skeleton of this system, the observed double bond twist angle is 16° .

The repulsion at short distances between inner hydrogens has been shown to reduce significantly the frequencies of the Me torsional modes in *cis*-2-butene.⁸ Similarly we find the same effect in tri- and tetramethylethylene. The calculated torsional frequencies of trimethylethylene are 206, 177 and 120 cm^{-1} . An inspection of the eigenvectors belonging to these frequencies indicates that the first one

is essentially a torsion of the Me group which is geminal to the inner Me group and interacts least with the other methyls. The two other torsional modes are rather analogous to the C_2 -antisymmetric and C_2 -symmetric methyl torsions of *cis*-2-butene (calculated values 179 and 132 cm^{-1} , respectively) which were discussed in detail previously.⁹ The shifts are more pronounced since the repulsion is stronger. The lowest of the two is that in which the amplitude of variation of the inner H...H distance is the largest. Durig *et al.*⁹ observed two bands at 219 and 178 cm^{-1} which they interpreted as the Me torsions assuming the former band to correspond to two normal modes. This latter assumption is not supported, however, by our calculations which suggest that the band of the lowest torsional mode was not observed by Durig *et al.* For tetramethylethylene we calculate the torsional frequencies 163, 162, 136, and 103 cm^{-1} . Here the molecular D_{2h} -symmetry implies a double minimum across the D_{2h} -conformational barrier, as noted above. The corresponding experimental modes proposed by Durig *et al.*⁹ are 227, 194, and 153 cm^{-1} . The source of the discrepancies is not clear.

Another effect of H...H interactions at short distance is to increase some of the Me C-H

stretching frequencies in *t*-Bu substituted ethylenes. Thus the highest calculated frequencies of this kind are 3011, 3026, and 3027 cm^{-1} in *cis*-1, 2-di-*t*-butylethylene, 2,3-di-*t*-butyl-*cis*-2-butene, and tri-*t*-butylethylene, respectively. For comparison the highest Me C-H stretching frequency in *trans*-1,2-di-*t*-butylethylene which does not contain short H...H contacts is 2982 cm^{-1} .

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