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Conformational analysis of some overcrowded olefins

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Chimica fisica. — *Conformational analysis of some overcrowded olefins* (*). Nota di ANGELO GAVEZZOTTI e MASSIMO SIMONETTA, presentata (**) dal Socio M. SIMONETTA.

RIASSUNTO. — Le strutture di equilibrio di tre olefine stericamente impedite sono state calcolate con la meccanica molecolare. Vengono discussi la torsione e l'allungamento del doppio legame, come pure l'influenza della geometria molecolare sulla molteplicità dello stato fondamentale.

The problem of torsion around a double bond in ethylene and substituted ethylenes has been approached in the past both theoretically and experimentally [1–4]. In particular, as the twist increases under the steric requirements of bulky substituents, the triplet state may become more stable than the singlet state, thus making the molecule unstable in the presence of air.

The so-called molecular mechanics method is well established as a powerful tool for predicting molecular conformations [5], and has been successfully applied to unconjugated [6] and conjugated [7] olefins. Of the compounds shown in fig. 1, I and III have recently been prepared [8], while II has not yet been synthesized. We have used Allinger's force field [7] for the calculation of the minimum-energy geometry for each of the three compounds in the singlet state. The Hückel method, modified to account for non-planarity [9, 10] was used to compute bond orders in I, the Extended Hückel method [11] was used to obtain the overlap populations for II and III; then a simple proportionality relationship was established between Hückel bond orders and Extended Hückel π overlap populations, using the standard results for ethylene, benzene, butadiene and naphthalene [11, 12]. In this way all necessary bond orders could be obtained for use according to the prescriptions of Allinger [7].

A reduction of the total number of degrees of freedom of the molecules was obviously needed. In I and II the ethylene frame was given all its 12 degrees of freedom. In I, the two phenyl rings have been considered as rigid hexagons, with edges 1.40 Å long, 120° angles and hydrogens on the bisector of each C—C—C angle at a distance of 1.10 Å from each carbon. Each hexagon was allowed three angular degrees of freedom. Each methyl carbon had three degrees of freedom; one additional torsional degree of freedom was given to each methyl group, corresponding to rotation about the pertinent C—C bond. The rest of the degrees of freedom of the methyl groups were reduced by the imposition of tetrahedral carbon and of equal C—H bond lengths.

(*) Work done at the Centro CNR and Institute of Physical Chemistry, University of Milan, Milan, Italy.

(**) Nella seduta del 15 novembre 1975.

In II, the four *t*-butyl groups were described by one C(ethylenic)—C(quaternary)—C(methyl) angle and one C(quaternary)—C(methyl) bond length, one C(quaternary)—C(methyl)—H angle and one C(methyl)—H bond length. These parameters were common to all the twelve methyl carbon atoms. In III the cages were considered as rigid fragments with dimensions given by an X-ray study of 1-bi(apocamphane) [13]. This assumption is perhaps the weakest point of our treatment, and the results for this molecule must be considered as preliminary. Table I compares the total number of degrees of freedom for each molecule with the number of degrees allowed.

TABLE I

Compound	Number of atoms, N	3 N-6	Number of degrees of freedom allowed
I	50	144	43
II	54	156	41
III	52	150	31

TABLE II

Compound	R (C=C)	AB dihedral angle	C_e — C_q	C_q — C_m	C=C—C_q	C — C_q — C_m	Relative energy
I	1.36	52	1.56	1.55	120	113	—
II	1.42	81	1.58	1.53	119	114 (*)	—
IIIa	1.38	32	1.55 (**)	1.55	128	116	0
IIIb	1.41	35	1.55 (**)	1.57	127	120	27
IIIc	1.38	27	1.55 (**)	1.56	128	119	6
IIId	1.39	36	1.55 (**)	1.55	127	122	10
IIIb	—	0	1.55 (**)	—	—	—	45(***)
IIId	1.38	0	1.55 (**)	1.58	127	123	24

(*) This value was made to be the same for all C —C_q—C_m angles. (**) Unoptimized value. (***) The energy minimization for this isomer was troublesome. This value is to be taken as very roughly approximate. For this reason, the geometrical parameters are not reported. For the carbons, *e* = ethylenic, *q* = quaternary, *m* = methyl. Entries in columns 4–7 are averages of sometimes rather different values. Angles in degrees, distances in Angstroms.

Figs. 2–3 and Table II show the essential results. In our calculations for I it appears that the energy minimum is surrounded by rather steep walls; this implies a rigidity of the molecule, which is expected to have in the crystal almost the same conformation as in the gas phase. The crystal structure analysis of I is being planned in this laboratory. For II the final geometry is as shown in fig. 3. The value of the twist angle, 81°, compares well with the one suggested by a study of some methyl- and *t*-butyl-substituted ethylenes by Lifson's CFF force field [14] (75°). Values shown in parenthesis in fig. 3 have

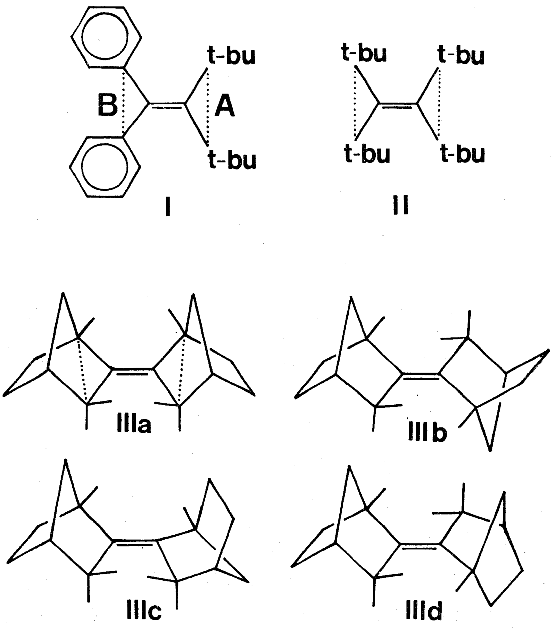
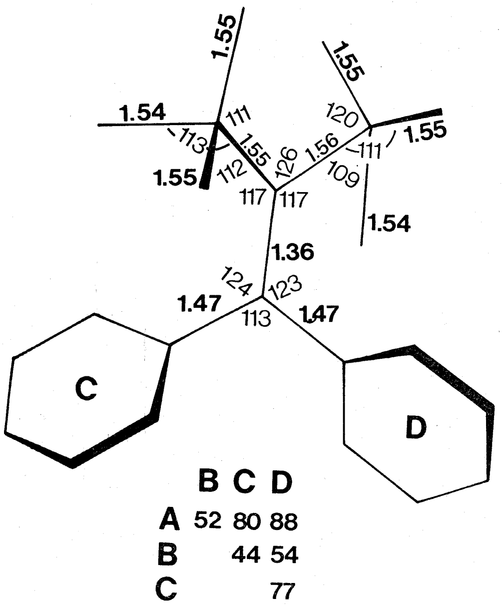


Fig. 1. – The compounds studied: I) 1,1-di-*t*-butyl-2,2-diphenylethylene; II) tetra-*t*-butylethylene; III) fenchylidenefenchane. Labels A and B in I refer to the planes defined by the three atoms joined by two C—C bonds and the dotted line. The same labeling applies to the like planes in II and III.



	B	C	D
A	52	80	88
B		44	54
C			77

Fig. 2. – The results for I. Distances in Å, angles in degrees. The table below refers to the dihedral angles between planes A, B (fig. 1), C, D (shown).

been obtained by means of the standard Allinger's force field for unconjugated hydrocarbons [6]. The use of this force field in the present case might be questioned since the central double bond is expected to have a geometry significantly different from a " natural " geometry. However, the results in both cases are quite similar. For IIIb and IIId calculations have been performed also imposing coplanarity of the A and B planes (fig. 1). Our calculations at the present stage suggest IIIa as the most stable isomer. For this compound too a crystal structure analysis is being planned.

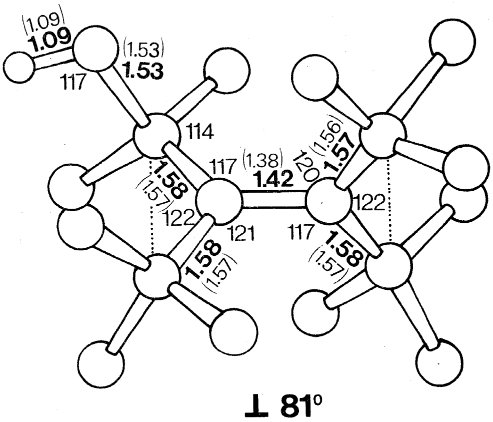


Fig. 3. – The results for II. Distances in Å, angles in degrees. The dihedral angle shown below is between planes A and B (fig. 1). For numbers in parenthesis, see text. No angular values in parenthesis are given, since they all coincide with the ones shown.

It is evident from the results shown that torsion around the double bond is mainly due to the presence of the *t*-butyl groups. For compound III the cage structure incorporates part of the strain that is found in II, where the *t*-butyl groups are free, and the twist angle is accordingly smaller. In compound I the rotation of the two phenyl rings is enough to meet much of the steric requirements, but a considerable twist (52°) is still necessary. For comparison, neither a bulky bromine in 2-bromo-1,1-di-*p*-tolylethylene [15] nor the four phenyl rings in tetraphenylethylene [16] can produce significant twist (0 and 8° respectively). In II, on the contrary, the most favourable way to release the strain is the twist, which assumes a value close to orthogonality.

If one considers now that the reported experimental curves of the energy of the singlet and triplet states of ethylene cross at least at 70° of twist [3, 17], this can be taken as an indication that also in substituted ethylenes the singlet is more stable below this value, and the triplet more stable above it. The ground state of II should then be a triplet state. The difficulties that arise in the synthesis of II may be related to the considerable strain energy of this compound: the calculated value is 91 or 97 Kcal mole^{-1} when the first or second method of calculation is used. Even if the triplet state lies below the singlet state by 1–2 eV (although the above mentioned curves show a much smaller difference) this molecule appears to have a high energetic content.

In conclusion, the strain imposed on the double bond increases in the order III $<$ I $<$ II, and seems to be correlated with the number of *t*-butyl groups connected to it.

From our calculations and the spectroscopic results for ethylene [3] it can be inferred that the ground state of compounds I and III should be singlet, and that of II triplet. The first two results are in agreement with experimental findings, while the third result is waiting for experimental confirmation.

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