Tetrahedron Letters,Vol.24,No.48,pp 5415-5418,1983 0040-4039/83 $3.00 + .00
Printed in Great Britain

ON THE PRESENCE OF EXTREMELY SHORT H...H NON-BONDED DISTANCES, AND ORBITAL INTERACTIONS THROUGH EIGHT σ BONDS OR THROUGH TWO METHYLENE GROUPS IN TETRAMETHANONAPHTHACENES.

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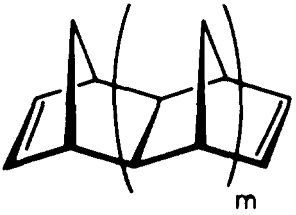
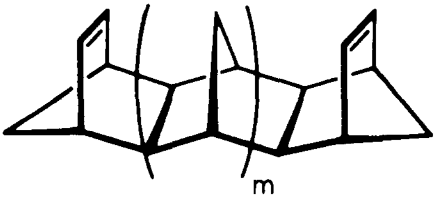
Summary: A joint molecular mechanics and molecular orbital study of the tetradecahydrotetramethanonaphthacenes 3 and 5 has revealed the presence of extremely short intramolecular non-bonded H...H distances, π orbital interactions through eight bonds, and the first example of σ-type orbital interactions through two methylene groups, the latter feature being confirmed by photoelectron spectroscopy.

The norbornylogous series of compounds,[1] illustrative of which are the lower members 1 - 5, is attracting interest of two different reasons:

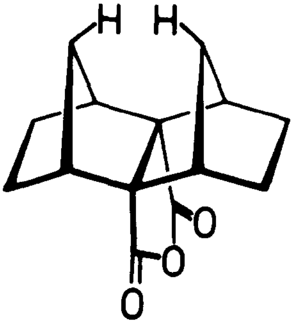


1 (m=1) **2** (m=2) **3** (m=3)



4 (m=1) **5** (m=2)

(1) Structural determinations of several decahydrodimethanonaphthalenes have revealed the presence of short C-H...H-C non-bonded contacts,[2] the current record holder being 6 in which the non-bonded distance between the indicated methylene hydrogens is only 1.713(4) Å by neutron diffraction.[3]



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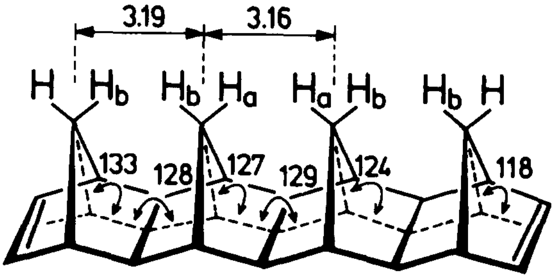

Figure.

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Some structural data of the all-trans compound 3 (C_2 form) calculated by MM2 (distances in Å and interplanar angles in degrees).

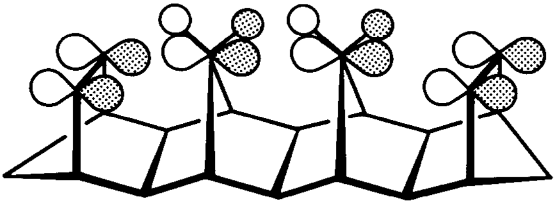
(2) Photoelectron spectroscopy of the norbornylogues 1, 2 and 4, have enabled Paddon-Row and his coworkers not only to verify that π orbital interactions through four and six bonds (OIT-4-B and OIT-6-B, respectively) are maximized for an all trans arrangement and are attenuated only mildly with increasing number of intervening σ bonds,[4] but also that the CH_2 group in 4 can act as a through bond relay in a new way, namely by a σ-type mixing.[5]

Herein are reported the preliminary results of our molecular mechanics and MO calculations on the norbornylogous 3 and 5, which reveal the presence of extraordinary steric and electronic properties for these compounds, as well as the photoelectron spectrum of 5.[6]

Complete geometry optimization with Allinger's MM2 molecular mechanics method[7] indicates that the all trans compound 3 prefers a "skewed" C_2 conformation with the methylene groups slightly turned away from each other. The C_{2v} conformation, which can be viewed as a formal transition state for the interconversion of the two enantiomeric C_2 conformations, has all four CH_2 groups in a plane and is placed 0.44 kcal/mol higher in energy. Some pertinent structural data are shown in the Figure. The two outer methylene groups in 3 are tilted outwards to minimize the strong H...H repulsion, a feature also observed by Ermer and Mason for 6.[3] Because this mode of relaxation is more difficult for the two inner methylene groups the $H_a...H_a$ distance (1.804 Å) is smaller than the $H_b...H_b$ distance (1.839 Å). The actual non-bonded separations are probably smaller than this since it has been shown[3] that MM2 as well as Ermer's consistent force field overestimated the actual C-H...H-C contacts in the related compound 6 by 0.13 Å. It therefore seems likely that the $H_a...H_a$ distance in 3 could be as small as 1.67 Å, an extremely short distance, to our knowledge the shortest encountered so far, and thus important for evaluation of molecular mechanics methods.[8]

The cis-trans-trans-cis isomer 5 exhibits a similar behavior with the C_{2v} conformation being 0.48 kcal/mol less stable than the C_2 conformation. The non-bonded C-H...H-C distance between the two methylene groups is calculated to be 1.807 Å for the C_2 conformation, which corresponds to a possible actual separation of 1.68 Å, again a very short distance.

MO calculations on the MM2 optimized structures of 3 and 5 were carried out using the PRDDO method.[9] The π,π splitting energy for 3 was calculated to be 0.05 eV. It is our experience[5] that the PRDDO MO method underestimates π OITB by as much as a factor of 2. It therefore seems likely that π OITB over eight sigma bonds in 3 could be as large as 0.1 eV and thus measurable. The calculated π,π splitting energy of 0.15 eV for 5 is even larger than that for 3, a result which appears to contradict the trans rule[4b] since the all trans arrangement of relaying sigma bonds, which is necessary for maximising OITB, is present in 3 but not in 5. However, this contradiction is only apparent since the π,π splitting energy for 5 is due to the mixing of the π MO's with the pseudo π MO's of the methylene group. PRDDO calculations reveal that the HOMO and SHOMO of 5 may be represented by 7 and 8, respectively. That the antisymmetric combination (π-π) of the π orbitals are destabilized slightly more by interaction with the out-of-phase combination of the two π_{CH_2} orbitals, $\pi_{CH_2}-\pi_{CH_2}$, (*i.e.* 7) than the symmetric (π+π) combination with the in-phase π_{CH_2} combination, $\pi_{CH_2}+\pi_{CH_2}$ (*i.e.* 8) is only due to the close spatial proximity of the methylene groups in 5 (*vide supra*). This will lead to the $\pi_{CH_2}-\pi_{CH_2}$ level lying higher than the $\pi_{CH_2}+\pi_{CH_2}$ level and therefore closer to the π manifold. These proposals are supported by the results of STO-3G *ab initio* calculations on the model ethene-methane-methane-ethene system 9, where the configuration mimics that of the corresponding groups in 5. Thus the π,π splitting energy for 9 is calculated to be 0.15 eV, in excellent agreement with the PRDDO result for 5. In the absence of the ethene units, the $\pi_{CH_2}-\pi_{CH_2}$ level is 1.75 eV higher than the $\pi_{CH_2}+\pi_{CH_2}$ level. In the absence of the methane units the π levels of the two ethenes are degenerate.



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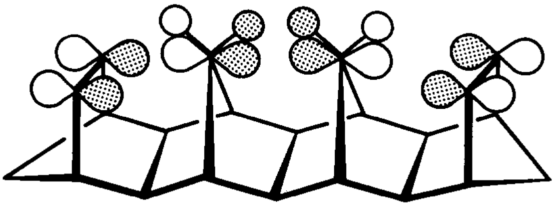

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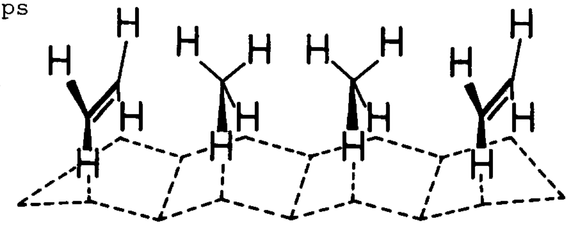

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The above calculations are nicely confirmed by the photoelectron spectrum of 5, which exhibits two low energy ionizations at 8.31 eV and 8.60 eV, respectively. The experimental π,π splitting energy on 0.29 eV for 5 is the first example of the just recently discovered[5] way of orbital interactions through a CH_2 group extended to interactions through two CH_2 groups.

Acknowledgements

We are grateful for financial support to M.N.P-R. from the Australian Research Grants Scheme and to F.S.J. from the Danish Natural Science Research Council.

References and Notes

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(Received in UK 22 September 1983)