Ab Initio Calculation on the Structure of the Bi(anthracene-9,10-dimethylene) Photoisomer: Is the Longest Known C–C Bond in This Molecule?

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Crystalline bi(anthracene-9,10-dimethylene) exists in three forms,[1–3] the α and β forms and a photoisomer (Figure 1). X-ray analysis has been performed on all of them, and it was concluded that the photoisomer has two highly strained four-membered rings with anomalously long C–C single bonds.[3] The distance of bond **a** (Figure 1) obtained from X-ray analysis, 1.77 Å, is perhaps the longest C–C single bond reported so far. This unusual bond length has been widely accepted, and several attempts to rationalize it have appeared.[4] A subsequent attempt was made to determine this bond length by neutron diffraction.[5] The authors state "attempted neutron diffraction analysis of a single crystal of [the compound] could not be brought to completion due to partial cycloreversion. However, the best possible guess for the central bond length [**a** 1.64(1) Å] was obtained." This anomalous C–C length could be partly attributed to the effect of hyperconjugation. Molecular mechanics calculations using an early version of the MM3(92) program which did not take into account the effect of hyperconjugation[6] resulted in the C–C bond length of 1.597 Å for this bond, while a recent version of the MM3 program (MM3(93)) which explicitly takes into account of the effect of hyperconjugation gives the C–C distance as 1.639 Å.[7] Thus hyperconjugation greatly lengthens this bond (by 0.042 Å), but nonetheless the calculated C–C bond length is still very much shorter than the experimental X-ray value, indicating that either the experimental result is in error or there are one or more other effects present that we do not know about and that have not been taken into account in the MM3(93) program. To clarify this question, we carried out ab initio calculations on the molecular structure of the photoisomer, and the results are reported herein.

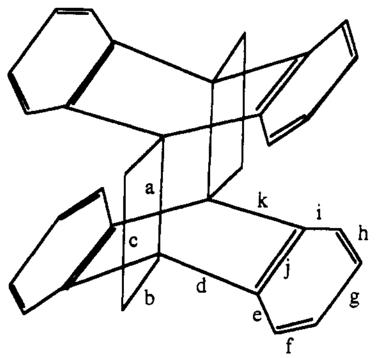

Figure 1. Schematic structure of bi(anthracene-9,10-dimethylene) photoisomer. The (3-21G) torsion angles in the four-membered rings are 14.6°, so the molecule has D_2 symmetry and not D_{2h} as in the schematic structure.

Table I. Comparison between the Calculated and X-ray C–C Distances[a] of the Bi(anthracene-9,10-dimethylene) Photoisomer

bond[b]	STO-3G	3-21G	MM3(93)	X-ray[c]
a	1.616	1.637	1.639	1.77
b	1.558	1.558	1.561	1.50
c	1.541	1.549	1.551	1.51
d	1.547	1.528	1.534	1.53
e	1.385	1.380	1.398	1.38
f	1.390	1.390	1.395	1.39
g	1.379	1.376	1.395	1.38
h	1.390	1.389	1.396	1.42
i	1.383	1.377	1.401	1.40
j	1.405	1.398	1.409	1.40
k	1.536	1.507	1.516	1.50

[a] Unit is Å. [b] The labeling of bonds is shown in Figure 1. [c] Reference 3.

Our complete geometry optimizations were carried out in internal coordinates using the geometry DIIS algorithm[8] at the restricted Hartree–Fock level (RHF) with both the STO-3G[9] and 3-21G[10] basis sets. For the title molecule, defining a set of proper nonredundant internal coordinates is not straightforward. To avoid this difficulty, we used a set of redundant internal coordinates defined according to the proposals of Pulay et al.[11] The optimizations were started with the MM3 geometry and terminated when the largest residual force was smaller than 2 × 10^{-4} mdyn. The MM3 structure has D_2 symmetry, but to avoid an artifact in the starting geometry of the STO-3G optimization, the molecule was distorted to have only C_2 symmetry. In agreement with the MM3 results, the calculation converged to a structure with D_2 symmetry. The D_2 symmetry was then used in the subsequent 3-21G geometry optimization. With both basis sets, the geometry optimization converged in about 15 steps.

The schematic structure of the target molecule is shown in Figure 1. The calculated C–C bond lengths are compared with the results of X-ray analysis and MM3 calculations in Table I. As the molecule has a large number of atoms, a complete listing of all the geometrical parameters is not given. However, the optimized STO-3G and 3-21G Cartesian coordinates are given in Tables S1 and S2 of the supplemental materials.

As is shown in Table I, the ab initio C–C bond distances are in excellent agreement with the recent MM3 calculations, but the calculated longest C–C bond distances (bond **a**) differ significantly from the result of the X-ray analysis.[5] The theoretical results are supported by the following facts. (1) The length of a carbon–carbon single bond between saturated carbons in simple molecules is about 1.54 Å. This length may be increased as a result of steric effects or other reasons. The bond length in a cyclobutane ring is somewhat longer, about 1.56 Å. Bond lengths still longer than this are not commonly found. (2) Although the ab initio method used here suffers from defects such as truncation of basis set and neglect of electron correlation, extensive comparisons between theoretical and experimental structures document that ab initio calculation at this level is a generally reliable tool for structural investigation of stable hydrocarbon compounds.[12]

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Known sources for the difference between the experimental and the ab initio bond lengths include that the theoretical results represent the equilibrium structure of an isolated molecule, while the experimental results are obtained for a vibrationally averaged molecule with interactions with other molecules in the crystal phase. These differences are known to be small, typically about 0.010 Å. Another error results from the truncated basis sets used and the lack of inclusion of electron correlation in the present calculations. To investigate the size of these errors, we optimized the structure of cyclobutane at the same theoretical level. The calculated STO-3G and 3-21G C–C distances of cyclobutane are 1.553 and 1.569 Å, respectively. The agreement between these results and the r_g and r_0 bond lengths of cyclobutane,[13,14] 1.555(3) and 1.558(3) Å, respectively, indicates that the calculated bond lengths are accurate to better than 0.02 Å. As the difference between the ab initio and the X-ray bond lengths of the photoisomer is so large (0.13 Å), it seems clear that the X-ray results are unreliable. On the other hand, the good agreement between the ab initio and the MM3(93) bond lengths (both 1.637 Å) indicates that the MM3(93) program satisfactorily takes into account of the effect of hyperconjugation on molecular structure, at least in this case. The agreement with the "best possible guess" from the neutron diffraction study is also good. We hope these results will stimulate new experimental studies on the structure of the title compound.

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Supplementary Material Available: Cartesian coordinates of ab initio STO-3G and 3-21G equilibrium structures of bi-(anthracene-9,10-dimethylene) photoisomer (2 pages). Ordering information is given on any current masthead page.

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