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Face-Fused Dicubane ($C_{12}H_8$) and Its Dicubene Isomer: Achievable Synthetic Targets?

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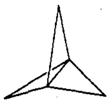
Contribution from the Center for Computational Quantum Chemistry, University of Georgia, Athens, Georgia 30602. *Received September 21, 1990*

Abstract: Dicubane and the much lower energy, structurally related isomer dicubene have been investigated with use of ab initio molecular quantum mechanical methods. With the double-ζ plus carbon d function (DZ+d) self-consistent-field (SCF) method, both structures are predicted to be minima on the $C_{12}H_8$ potential energy hypersurface. Several comparisons with the known $C_{12}H_8$ isomers acenaphthylene and biphenylene are made. Dicubane and dicubene represent two beautifully symmetrical, significant highly strained challenges to synthetic organic chemists. The strain energy of dicubane is more than twice that of the experimentally characterized cubane molecule.

The history of organic chemistry is replete with stories of supposedly unmakeable molecules that have in fact been subsequently synthesized. An important recent example is [1.1.1]-propellane.[1,2]



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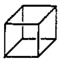
[1.1.1]Propellane is particularly interesting in the present context since all four bonds to each bridgehead carbon atom lie in a hemisphere. In one sense more closely related to the present research are Eaton and Cole's 1964 synthesis[3] of cubane



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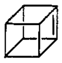
and the more recent syntheses of cubene[4]



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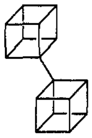
cubylcubane[5]



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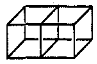
and the cubyl cation.[6,7] Perhaps the most fascinating feature of cubene (**3**) is that all three carbon–carbon bonds (with respect to each of the doubly bonded carbon atoms) lie roughly within an octant of solid geometrical space. Practically speaking, this means that the two "unprotected" carbon atoms in cubene will be highly reactive.

In this paper, we address the question of a more intimate union of two cubane moieties than is present in the recently synthesized cubylcubane molecule (**4**). Specifically, we examine the $C_{12}H_8$ potential energy hypersurface in the region of the species



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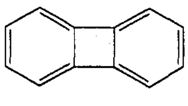
to which we give the common name "dicubane". To our knowledge, the existence of such a species has never been suggested in the chemical literature. In addition to being beautifully symmetrical, dicubane would certainly be among the most severely strained organic molecules synthesized to date.

Figure 1 contains theoretical predictions for the equilibrium geometry of dicubane at the ab initio self-consistent-field (SCF) level of theory using three basis sets: (a) the STO-3G minimal basis;[8] (b) the Huzinaga–Dunning[9,10] double-ζ (DZ) basis set designated C(9s5p/4s2p) H(4s/2s); and (c) the DZ+d basis obtained by appending a set of d functions (orbital exponent = 0.75) to each carbon atom. This DZ+d basis set includes 196 contracted Gaussian basis functions for $C_{12}H_8$. All three theoretical methods normally give reliable predictions for the equilibrium geometries of hydrocarbons.[11]

The bond distances in dicubane are both shorter and longer than the 1.55 Å observed[12] in cubane (**2**) itself. The DZ+d SCF values for the four central (or "unprotected") bonds are 1.504 Å, while those for the eight outer C–C bonds are 1.595 Å. The latter would rank among the longest known carbon–carbon single bonds and are seemingly indicative of the general instability of dicubane compared to normal saturated hydrocarbons. The eight intermediate C–C bonds are of length 1.577 Å, i.e., long but not abnormally so.

At all three levels of theory dicubane is a genuine minimum on the $C_{12}H_8$ potential energy hypersurface. At the highest level of theory (DZ+d SCF) the predicted harmonic vibrational frequencies are displayed in Table I. The lowest predicted harmonic vibrational frequency is 386 cm^{-1}. Two of the C–H stretching vibrational frequencies, ω_{24} (A_{2u}) and ω_{35} (E_u), should be prominent in the infrared spectrum due to their high intensities. Of course the theoretical frequencies should be reduced by about 10% to reflect the effects of electron correlation and anharmonicity.

Among plausible products of the unimolecular reaction of dicubane, the second lowest in energy that we have structurally optimized is biphenylene



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We predict that biphenylene lies 316 kcal/mol below dicubane. Although this result underscores the fact that dicubane is a highly energetic species, the reader should note that the readily synthesized cubane molecule (**2**) has an experimental strain energy of no less than 157 kcal/mol.[1]

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[1] Molecule **1** was commonly predicted not to exist. See, for example: Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Academic Press: New York, 1978.

[2] Wiberg, K. B.; Walker, F. H. *J. Am. Chem. Soc.* **1982**, *104*, 5239. For an excellent review, see: Wiberg, K. B. *Chem. Rev.* **1989**, *89*, 973.

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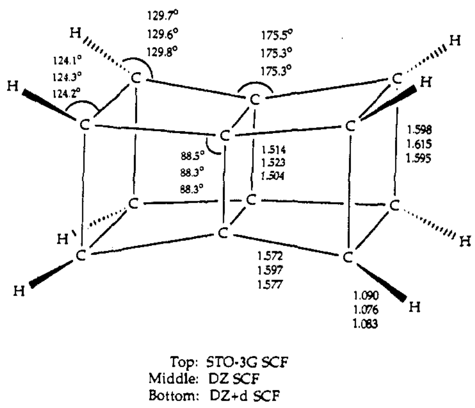
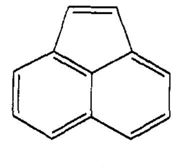


Figure 1. Ab initio quantum mechanical predictions of the equilibrium geometry of dicubane (**5**, $C_{12}H_8$) at three levels of theory. All bond distances are in Å.

Table I. Harmonic Vibrational Frequencies (cm^{-1}) and Relative IR Intensities for the Equilibrium Structure of Dicubane at the DZ+d SCF Level of Theory

		freq	rel IR intensity
A_{1g}	ω_1	3306	0
	ω_2	1383	0
	ω_3	1229	0
	ω_4	946	0
	ω_5	713	0
A_{2g}	ω_6	1279	0
	ω_7	802	0
B_{1g}	ω_8	1288	0
	ω_9	1152	0
	ω_{10}	904	0
B_{2g}	ω_{11}	3278	0
	ω_{12}	1301	0
	ω_{13}	1110	0
	ω_{14}	809	0
	ω_{15}	674	0
E_g	ω_{16}	3288	0
	ω_{17}	1342	0
	ω_{18}	1285	0
	ω_{19}	1124	0
	ω_{20}	857	0
	ω_{21}	724	0
A_{1u}	ω_{22}	1275	0
	ω_{23}	513	0
A_{2u}	ω_{24}	3302	100.0
	ω_{25}	1314	4.8
	ω_{26}	1222	0.01
	ω_{27}	905	3.7
B_{1u}	ω_{28}	3278	0
	ω_{29}	1331	0
	ω_{30}	1209	0
	ω_{31}	966	0
	ω_{32}	742	0
B_{2u}	ω_{33}	1190	0
	ω_{34}	895	0
E_u	ω_{35}	3288	59.7
	ω_{36}	1338	1.7
	ω_{37}	1310	0.3
	ω_{38}	1209	1.0
	ω_{39}	889	0.3
	ω_{40}	857	2.1
	ω_{41}	386	6.0

The global minimum for the $C_{12}H_8$ is probably the acenaphthylene molecule



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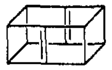
Acenaphthylene is predicted to lie 354 kcal/mol below dicubane, or 38 kcal/mol below biphenylene. For comparison acenaphthylene is considered experimentally to lie 37.8 ± 1.9 kcal below biphenylene. Thus the energetic predictions at the DZ+d SCF level of theory appear qualitatively reasonable.

Table II. Harmonic Vibrational Frequencies (cm^{-1}) and Relative IR Intensities for the Equilibrium Structure of Dicubene at the DZ+d SCF Level of Theory

		freq	rel IR intensity
A_g	ω_1	3314	0
	ω_2	1783	0
	ω_3	1333	0
	ω_4	1245	0
	ω_5	1041	0
	ω_6	965	0
	ω_7	782	0
	ω_8	541	0
B_{1g}	ω_9	3284	0
	ω_{10}	1398	0
	ω_{11}	1300	0
	ω_{12}	1048	0
	ω_{13}	913	0
	ω_{14}	709	0
	ω_{15}	484	0
B_{2g}	ω_{16}	3296	0
	ω_{17}	1389	0
	ω_{18}	1294	0
	ω_{19}	1235	0
	ω_{20}	1016	0
	ω_{21}	783	0
B_{3g}	ω_{22}	3293	0
	ω_{23}	1433	0
	ω_{24}	1306	0
	ω_{25}	1252	0
	ω_{26}	875	0
	ω_{27}	462	0
A_{1u}	ω_{28}	3282	0
	ω_{29}	1430	0
	ω_{30}	1326	0
	ω_{31}	1227	0
	ω_{32}	1007	0
	ω_{33}	771	0
	ω_{34}	416	0
B_{1u}	ω_{35}	3309	100.0
	ω_{36}	1326	0.04
	ω_{37}	1297	4.0
	ω_{38}	1193	5.5
	ω_{39}	962	0.3
	ω_{40}	933	0.7
B_{2u}	ω_{41}	3294	47.8
	ω_{42}	1781	32.7
	ω_{43}	1481	1.9
	ω_{44}	1287	3.5
	ω_{45}	929	1.8
	ω_{46}	915	0.3
	ω_{47}	704	19.1
B_{3u}	ω_{48}	3298	63.3
	ω_{49}	1329	4.2
	ω_{50}	1296	3.4
	ω_{51}	1076	0.7
	ω_{52}	840	0.01
	ω_{53}	634	27.0
	ω_{54}	463	7.5

Among other isomers of $C_{12}H_8$ that we have examined, it is of interest to note that the unknown unsaturated species



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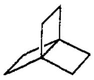
designated dicubene here, is predicted to lie 122 kcal/mol (DZ+d SCF method) below dicubane. Among organic chemists we have consulted, there seems to be agreement that the most likely channel for the disappearance of dicubane (**5**) is the unimolecular rearrangement to dicubene (**8**). However, dicubene itself is a species possibly even more fascinating than dicubane, and certainly likely to be synthesized prior to dicubane.

The predicted DZ+d SCF molecular structure for dicubene is shown in Figure 2. It is important to note that, although dicubane (**5**) and dicubene (**8**) appear very similar structurally from the simple cube-based sketches in the text of this paper, in fact Figures 1 and 2 show them to be rather different. Since two, rather than four, carbon–carbon bonds fuse the two halves of the molecule in dicubene, dicubene occupies a much larger volume of space than does dicubane. This result is reinforced by the results of an evaluation of the total energy of dicubene at the dicubane equilibrium geometry. This exercise shows dicubene to lie 295 kcal/mol higher, i.e., dicubane is *not* a doubly excited electronic state of dicubene at the equilibrium geometry of the former.

DZ+d SCF vibrational frequencies and IR intensities are given for dicubene in Table II, which proves that dicubene is a genuine minimum on the $C_{12}H_8$ potential energy hypersurface at this level of theory. As with the much higher energy dicubane molecule, dicubene has several C–H vibrational stretching frequencies with significant IR intensities, namely $\omega_{35}(B_{1u})$, $\omega_{41}(B_{2u})$, and $\omega_{48}(B_{3u})$.

The question of the existence of a barrier between **5** and the lower energy **8** cannot be unambiguously settled at the single configuration self-consistent-field level of theory. Some sort of post-Hartree–Fock theoretical treatment will be required for this purpose. However, the theoretical delicacy of such a barrier is illustrated by the research of Feller and Davidson[13] on the [2.2.2]propellane



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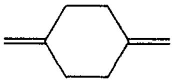
rearrangement to dimethylenecyclohexane



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Although Feller and Davidson report that the two-configuration SCF method predicts the stability of **9** to ring opening, their higher level configuration interaction (CI) method finds no minimum for [2.2.2]propellane. Experimentally, Eaton and Temme[14] have in fact isolated the dimethylcarboxamide derivative of [2.2.2]-propellane. We conclude that theoretical efforts to predict the absolute stability of dicubane (**5**) would not be profitable at this time. This issue notwithstanding, the lower energy dicubene (**8**) remains an attractive synthetic target.

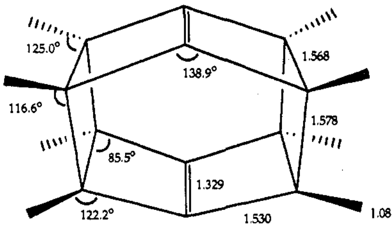
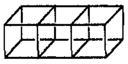


Figure 2. Predicted equilibrium geometries for the dicubene molecule (**7**, $C_{12}H_8$). All bond distances are in Å.

Should dicubane or some more favorable derivative (presumably one for which bulky R groups defend the four "unprotected" carbon atoms) be synthesized, one's imagination can readily construct a family of related molecules,[15] the first member of which might be called "tricubane".



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Of course, as the fused-cube structures in this family become longer, the eight R groups on the ends will become increasingly ineffective in protecting the highly strained interior carbon atoms.

Acknowledgment. This research was supported by the U.S. National Science Foundation, Grant CHE-8718469. We thank Professors Norman Allinger, Weston Borden, Philip Eaton, Joel Liebman, and Josef Michl for helpful comments and suggestions. Dicubane is under active consideration (private communication, May 3, 1990) by the Eaton group concerning its possible synthesis. We thank Professor Reinhart Ahlrichs for use of the TURBOMOLE system of programs.

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Dinitrogen Sulfide (N_2S) and Its Protonated Isomers

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Contribution from the Center for Computational Quantum Chemistry, University of Georgia, Athens, Georgia, 30602. *Received August 29, 1990*

Abstract: The protonation of N_2S offers a way of examining the nature of this simple, recently synthesized molecule. The conventional linear NNS, the less conventional NSN, and cyclic structures have been investigated with ab initio molecular quantum mechanical methods. Double-ζ plus polarization (DZP) and triple-ζ plus double polarization (TZ2P) basis sets have been used in conjugation with self-consistent-field (SCF), single and double excitation configuration interaction (CISD), and coupled cluster (CCSD) methods. The parent N_2S potential energy hypersurface is rather complicated, but for the protonated system no isomer lies within 30 kcal/mol of the $NNSH^+$ global minimum.

Introduction

Although Powell[1] postulated the existence of N_2S in 1975 it was not until 1986 that Wentrup, Fischer, Maquestiau, and Flammang confirmed (via mass spectroscopy) the presence of N_2S as a decomposition product.[2] They also recorded an infrared band at 2030 cm^{-1} which they assigned to the N–N stretch. Earlier Kass and DePuy had postulated that the reaction

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[†] Present address: Department of Chemistry Liberty University, Lynchburg, VA 24502.

[1] Powell, F. X. *Chem. Phys. Lett.* **1975**, *33*, 393.

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