Ab Initio Calculations of the Relative Energies of 1,2-, 1,3-, and 1,4-Dehydrocubane: Prediction of Dominant Through-Bond Interaction in 1,4-Dehydrocubane

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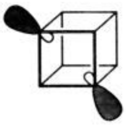
Recently we reported the results of ab initio calculations of the hydrogenation energy of 1,2-dehydrocubane (cubene, **1**) to cubane.[1] Our calculations indicated that, despite the presence of the highly pyramidalized double bond in **1**, the molecule should be preparable. This prediction was subsequently confirmed by the synthesis of **1** by Eaton and Maggini[2] and by the preparation of the closely related alkene, homocubene, by us[3] and, independently, by Schafer and Szeimies.[4]


1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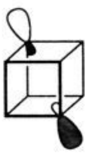
3


4

In this communication, we report the results of calculations of the energies of two isomers, **2** and **3**, of **1**, relative to that of **1**. We find that the energy difference between **1** and **2** is sufficiently small to suggest that **2** might be preparable by the same type of reaction (reductive dehalogenation) used for the synthesis of **1**.[2-4] Our calculations also predict that, unlike the case in **1** and **2**, where the dominant interaction[5] between the two, weakly bonded, AOs is through-space, in **3** the dominant interaction between these AOs is through the σ bonds of the cubane skeleton.

Geometries were optimized with the 3-21G basis set.[6] Because of the substantial amount of diradical character expected in **1**–**3**, two-configuration (TC) SCF wave functions were employed,[7] using the GVB option in Gaussian 86.[8] Vibrational analyses showed all three didehydrocubanes to be minima. Energies at the 3-21G optimized geometries[9] were recalculated with the 6-31G* basis set;[10] the relative TCSCF energies with both basis sets are given in Table I. Also listed for comparison are the ROHF energies at the UHF 3-21G optimized geometries[9] of the lowest triplet states of **1**–**3**.[11]

At the TCSCF optimized geometry for 1,3-dehydrocubane (**2**),[9] the C_1–C_3 distance of 2.086 Å is 0.11 Å shorter than that in the geometry optimized for the lowest triplet state of **2**. The TCSCF energy of the singlet is 17.3 kcal/mol lower than the ROHF energy of the triplet. Additional evidence for significant bonding in **2** between C_1 and C_3 comes from the ratio of 4.07 for the squares of the two coefficients in the TCSCF wave function. This is less than the ratio of 7.03 in the TCSCF wave function for **1** but substantially larger than the ratio of unity that would be found were **2** truly a diradical.[7]

Table I. Relative Energies (kcal/mol) of the Lowest Singlet and Triplet States of **1**–**4** at Geometries[a] Optimized with the 3-21G Basis Set

molecule	3-21G TCSCF singlet	6-31G* TCSCF singlet	6-31G* ROHF triplet
1	0[b]	0[c]	26.1
2	7.4	8.1	25.4
3	11.7	15.4	25.7
4	12.4[d]	11.7[d]	

[a] TCSCF geometries for singlets and UHF geometries for triplets. [b] $E = -304.4348$ hartrees. [c] $E = -306.1386$ hartrees. [d] Geometry optimized and energy calculated with two GVB pairs.

Although the C_1–C_3 distance in **2** is 0.662 Å longer than the C_1–C_2 distance of 1.424 Å in **1**,[1] the 6-31G* TCSCF energy of **2** is only 8.1 kcal/mol higher than that of **1**. The similarity between the energies calculated for the two isomers suggests that, like **1**,[2] **2** might be preparable by reductive dehalogenation of a diiodide precursor.

In 1,4-dehydrocubane (**3**),[9] the C_1–C_4 distance is 2.686 Å. This is too long to allow substantial through-space interaction between the AOs at these carbons, and, in fact, the dominant configuration in the TCSCF wave function for **3** has the out-of-phase ($5a_{2u}$) combination of AOs at these two carbons, rather than the in-phase ($6a_{1g}$) combination, doubly occupied. The preferential occupancy of $5a_{2u}$ indicates that the interaction of the AOs with the C–C bonds of the cubyl skeleton dominates the direct interaction of the AOs through space.

Calculations[13] on [2.2.2]propellane[14] have shown that the competition between through-bond and through-space interactions between the AOs at C_1 and C_4 results, at the TCSCF level of theory,[13c] in a potential surface with two minima. In order to ascertain whether on the TCSCF potential surface for **3** there was a second minimum, where through-space interaction between the AOs at C_1 and C_4 was dominant, a geometry was optimized for a 3-21G SCF wave function with $6a_{1g}$ doubly occupied. At this geometry the C_1–C_4 distance was 1.980 Å, but the 3-21G TCSCF energy was 91.0 kcal/mol above that at the TCSCF minimum. Starting from this point, TCSCF geometry reoptimization led back to the previously located TCSCF energy minimum.

The ratio of the squares of the two coefficients in the TCSCF wave function at the optimized geometry for **3** is 1/2.70. This ratio indicates that **3** has appreciably more diradical character than **2**. Not surprisingly, therefore, the 6-31G* TCSCF energy of **3** is computed to be 7.3 kcal/mol above that of **2**. Nevertheless, evidence for a stabilizing interaction between C_1 and C_4 in **3** comes from the fact that the TCSCF energy of the singlet is 10.3 kcal/mol lower than the ROHF energy of the triplet.

Should **3** be formed, it could conceivably undergo an orbital symmetry allowed[12a] cleavage of a C–C bond, to afford diene **4**. Since **4** contains two bridgehead double bonds, we optimized its geometry, using a wave function with two GVB pairs, so that the "π" electrons in each strained double bond were correlated.[9] The same type of wave function was used to recompute the energy of **4** with the 6-31G* basis set at the optimized 3-21G geometry.

As shown in Table I, with both basis sets, the energy of **3** is calculated to be very close to that of **4**. Since we correlated one more pair of electrons in **4** than in **3**, the energetic proximity of **3** and **4** at this level of theory suggests that **3** is actually the lower in energy. Nevertheless, although the cleavage of **3** to **4** may not be thermodynamically favorable, the possibility remains that reductive dehalogenation of a potential precursor of **3** could lead,

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(1) Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1988**, *110*, 4710.

(2) Eaton, P. E.; Maggini, M. *J. Am. Chem. Soc.* **1988**, *110*, 7230.

(3) Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1988**, *110*, 7229.

(4) Schafer, J.; Szeimies, G. *Tetrahedron Lett.* **1988**, *29*, 5253.

(5) Hoffmann, R.; Imamura, A.; Hehre, W. J. *J. Am. Chem. Soc.* **1968**, *90*, 1499. Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1.

(6) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939.

(7) Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92. Borden, W. T. In *Diradicals*; Borden, W. T., Ed.; Wiley: New York, 1982; pp 1–72.

(8) Frisch, M.; Binkley, J. S.; Schlegel, J. B.; Raghavachari, K.; Martin, R.; Stewart, J. J. P.; Bobrowicz, F.; Defrees, D.; Seeger, R.; Whiteside, R.; Fox, D.; Fluder, E.; Pople, J. A., Carnegie-Mellon University.

(9) Available as supplementary material; ordering information is given on any current masthead page.

(10) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 212.

(11) Comparison of triplet ROHF (but not UHF) energies with singlet TCSCF energies provides a measure of bond energies. For example, the difference of 64.2 kcal/mol between the 6-31G* ROHF energy of −77.9580 hartrees at the equilibrium triplet geometry (D_{2d}) of ethylene and the TCSCF energy of −78.0603 hartrees for the planar (D_{2h}) singlet ground state is in excellent agreement with the experimentally measured[12] π bond dissociation energy of ethylene.

(12) Douglas, J. E.; Rabinovitch, B. S.; Looney, F. S. *J. Chem. Phys.* **1955**, *23*, 315.

(13) (a) Stohrer, W.; Hoffmann, R. *J. Am. Chem. Soc.* **1972**, *94*, 779. (b) Newton, M. D.; Schulman, J. M. *J. Am. Chem. Soc.* **1972**, *94*, 4391. (c) Feller, D.; Davidson, E. R. *J. Am. Chem. Soc.* **1987**, *109*, 4133.

(14) Eaton, P. E.; Temme, G. H. *J. Am. Chem. Soc.* **1973**, *95*, 7508.

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instead, directly to **4** by Grob fragmentation.

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Registry No. 1, 124225-53-2; **2**, 124225-54-3; **3**, 124225-34-9; **4**, 124225-55-4.

Supplementary Material Available: Singlet TCSCF and triplet UHF optimized 3-21G geometries for **1**–**3** and the 3-21G geometry for singlet **4**, optimized with two GVB pairs (7 pages). Ordering information is given on any current masthead page.

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(15) Eaton, P. E.; Tsanaktsidis, J. *J. Am. Chem. Soc.* Third of three papers in this issue.

(16) Hassenrück, K.; Radziszewski, J. G.; Balaji, V.; Murthy, G. S.; McKinley, A. J.; David, D. E.; Lynch, V. M.; Martin, H.-D.; Michl, J. *J. Am. Chem. Soc.* First of three papers in this issue.

The Reactions of 1,4-Dihalocubanes with Organolithiums. The Case for 1,4-Cubadiyl

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Recently Eaton and Maggini reported that reaction of 1,2-diiodocubane with *tert*-butyllithium produces 1,2-dehydrocubane (cubene).[1] We report now our work on the reactions of 1,4-dihalocubanes with organolithiums undertaken in search of "1,4-dehydrocubane".[2]

Addition of 1,4-diiodocubane[3] in THF to an excess of *tert*-butyllithium in THF/pentane at −78 °C followed by carbomethoxylation[4] gives primarily 1,4-dicarbomethoxycubane (from 1,4-dilithiocubane, **2**) and **5** in a ratio of ca. 2:1 (Scheme I).[5] The latter comes via elimination of HI from 4-iodolithiocubane (**1**) giving 4-lithiocubene (**3**), followed by addition of *tert*-butyllithium to this strained olefin (→**4**).[1] No substantial amounts of bicubyls are found. On the other hand, dropwise addition of *tert*-butyllithium *to* a solution of 1,4-diiodocubane in THF at −78 °C followed by carbomethoxylation gives a diverse mixture of products including 4-*tert*-butylcarbomethoxycubane (**6**), 4,4′-dicarbomethoxybicubyl (**7**),[6] and 4-carbomethoxybicubyl (**8**)[5a,7,8] (Scheme II); **6** and the bicubyls **7** and **8** are thought to arise, respectively, from reaction of *tert*-butyllithium, (iodocubyl)lithium (**1**), or cubyllithium with 1,4-dehydrocubane.

When 1,4-dibromocubane or 4-bromoiodocubane is used in place of the 1,4-diiodide in either mode of addition, the principal products are derived via lithiocubene **3**. The rate of formation of 1,4-dehydrocubane by loss of LiBr from 4-bromolithiocubane is apparently slow by comparison to loss of LiI from **1**, as is the rate of bromine–lithium exchange. Evidently, *tert*-butyllithium-induced dehydrobromination (→**3**) can compete effectively. Reaction of 4-chloroiodocubane with *tert*-butyllithium in THF at −78 °C gives 4-chlorolithiocubane. This halolithiocubane is stable at this temperature; it is trapped effectively by carboxylation.

Dropwise addition of *n*-butyllithium (2 equiv) to 1,4-diiodocubane *in ether* at 0 °C followed by carbomethoxylation gives 4.4′-dicarbomethoxybicubyl (**7**, 30% isolated yield) and a little 4-*n*-butylcarbomethoxycubane (**9**).[5a,8] When the addition order is reversed, **9** predominates over **7**. When 4-bromo- or 4-chloroiodocubane was used, similar behavior was observed, but the diester **7** was replaced with halo ester **10** (X = Br or Cl, Scheme III).

We know from the behavior of monohalocubanes that direct alkyllithium/halocubane coupling or halogen–metal exchange followed by coupling cannot account for the products formed in reactions of the dihalides. Iodocubane undergoes ready halogen–metal exchange with *n*- or *tert*-butyllithium, but little (*n*-butyl) or no coupling (*tert*-butyl) product is formed. Bromocubane does not undergo halogen–metal exchange or coupling noticeably with *n*-butyllithium in ether at 0 °C; an even greater lack of reactivity can be expected for chlorocubane.

The disparate behavior of the individual monohalocubanes toward *n*-butyllithium contrasts sharply with the similar behavior observed within the set of the 4-haloiodocubanes. It seems likely therefore that, after initial lithium-for-iodine exchange (→**11**), a common halogen-free intermediate is formed. As 1,4-dilithiocubane (**2**, see Scheme I) is not reactive in Wurtz-type coupling reactions, we propose that formation of **11** is followed by its slow decomposition to 1,4-dehydrocubane. This very reactive intermediate is trapped by *n*-butyllithium, when present in excess. Otherwise, it is trapped instead by yet undecomposed **11**. The 4′-halolithiobicubyl so formed remains as such until quenched or, in the case of X = I, undergoes iodine–metal exchange, to give 4,4′-dilithiobicubyl and ultimately the diester **7**.[9]

The intermediacy of a halogen-free species in these reactions was confirmed on finding that treatment of any of the 4-X-iodocubanes (X = I, Cl, or Br) with excess phenyllithium in ether at room temperature gives the same product, 4-phenyliodocubane (**12**, mp 84.5–85 °C), in good yield.[10] These reactions must be initiated by iodine-for-lithium exchange (generating iodobenzene); subsequent loss of LiX gives 1,4-dehydrocubane; phenyllithium adds to it, and the product is iodinated by reverse Li-for-I exchange with iodobenzene (Scheme IV).[11]

To test for the presence of a symmetric intermediate, we synthesized[12] specifically labeled 2-deuterio-4-bromoiodocubane and

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(1) Eaton, P. E.; Maggini, M. *J. Am. Chem. Soc.* **1988**, *110*, 7230.

(2) The formation of single bonds in highly strained molecules by through-space dehalogenation has a checkered history. Claims for formation of [2.2.2]propellane from a 1,4-dihalobicyclo[2.2.2]octane by electrolysis (Wiberg, K. B.; Epling, G. A.; Jason, M. *J. Am. Chem. Soc.* **1974**, *96*, 912) or by reaction with *tert*-butyllithium (Wiberg, K. B.; Pratt, W. E.; Bailey, W. F. *J. Am. Chem. Soc.* **1977**, *99*, 2297) have been withdrawn (Wiberg, K. B.; Pratt, W. E.; Matturro, M. G. *J. Org. Chem.* **1982**, *47*, 2720. See also: Adcock, W.; Iyer, V. S.; Kitching, W.; Young, D. *Ibid.* **1985**, *50*, 3706). There is evidence for the formation of [2.2.1]propellanes (Walker, F. H.; Wiberg, K. B.; Michl, J. *J. Am. Chem. Soc.* **1982**, *104*, 2056 and references therein) and [2.1.1]propellanes (Wiberg, K. B.; Walker, F. H.; Pratt, W. E.; Michl, J. *Ibid.* **1983**, *105*, 3638) by dehalogenation of the appropriate bridgehead diiodides. [1.1.1]Propellane has been made from 1,3-dibromobicyclo[1.1.1]pentane and fully characterized (Wiberg, K. B.; Walker, F. H. *Ibid.* **1982**, *104*, 5239). The formation of trishomo[2.2.2]propellane (or "its diradical or zwitterionic equivalent") has been suggested to account for the chemistry of 1,5-diiodotrishomobarrelene (de Meijere, A. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 809).

(3) (a) Tsanaktsidis, J.; Eaton, P. E. *Tetrahedron Lett.* In press. (b) Della, E. W.; Tsanaktsidis, J. *Aust. J. Chem.* **1989**, *42*, 61.

(4) Quenching with CO_2, acidification, and diazomethane esterification.

(5) (a) Not insignificant amounts of various reduction products are also formed. (b) Small amounts of 2- and 3-*tert*-butylcarbomethoxycubanes are formed, probably from partial protonation of **4** prior to carboxylation. Some 4-*tert*-butylcarbomethoxycubane is also produced, most likely arising from 1,4-dehydrocubane. (c) The structures of these products and others reported here were determined by mass spectroscopy and analysis of the high-field NMR spectra.

(6) The structure of **7**, the first 4,4′-disubstituted bicubyl, was confirmed by single-crystal X-ray diffraction (Eaton, P. E.; Tsanaktsidis, J.; Pramod, K.; Gilardi, R. Manuscript in preparation). Cf.: Gilardi, R.; Maggini, M.; Eaton, P. E. *J. Am. Chem. Soc.* **1988**, *110*, 7232.

(7) Including 4-(α-tetrahydrofuranyl)carbomethoxycubane, whose origin is obscure; it is not seen in any of the other experiments reported here.

(8) Quenching with methanol gives the corresponding compounds with H in place of CO_2Me; e.g., bicubyl, mp 178–180 °C,[1] was isolated in 42% yield.

(9) The bicubyllithiums can, and do, add to 1,4-dehydrocubane, producing oligomeric cubanes.

(10) Reduction fortunately is much less a problem here (cf. ref 5a). We thank D. S. Reddy and A. Bashir-Hashemi for early experiments into these reactions.

(11) Reaction of cubyllithium with iodobenzene in ether at room temperature generates iodocubane cleanly. Phenyllithium and iodocubane do not react under these conditions.

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