rate (Table I, entries 1-3, 5, and 6, and Figure 1),[6] indicative of Newtonian behavior.

The addition of PVME or PPO (both in 0.5 g dL^{-1} concentrations) completely changes the solution characteristics of the CTAB/NaSal solution. The viscosity is reduced by several orders of magnitude to a water-like value, and no viscoelasticity can be observed either visually or rheometrically. These data suggest a complete transition from rodlike to spherical micellar aggregates.[7] Presumably, this morphological transition is driven by the tendency of sufficiently hydrophobic polymers to wrap around the surface of surfactant aggregates, thereby reducing the unfavorable core-water contact at the surface of the assembly.[8,10,15] Since the surface/volume ratio is larger for spherical micelles than for rods, the presence of PVME or PPO leads to preferred sphere formation.[15] No such effect is found for PEO or PVP (Figure 1, Table I). The viscoelasticity of the CTAB/NaSal solution in the presence of PEO at shear rates ranging from 0.119 to 3808 s^{-1} is slightly increased as indicated by the first normal stress difference (cone-and-plate geometry). This is probably related to the enhanced viscosity of the CTAB/NaSal/PEO system in this range of shear rates. Thus the presence of PEO does not greatly affect the rodlike structures, although modest effects on the exact rheological properties are revealed. The same conclusion holds for PVP.

In summary, the present results show that micelle-polymer interactions can have a dramatic effect on the morphology of the surfactant assembly and can completely change the rheological behavior of the solution. Further studies in this field are in progress.

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A Body-Diagonal Bond in Cubane: Can It Be Introduced?

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1,4-Dihalogenated norbornanes and bicyclo[2.1.1]hexanes react with alkali metal vapors[2] to yield [2.2.1]propellane[3] and [2.1.1]propellane.[4] Can a body-diagonal bond be introduced into cubane? Like [1.1.1]propellane,[5] **1** might lead to staff-like oligomers[6-9] and polymers.[6,8,10]

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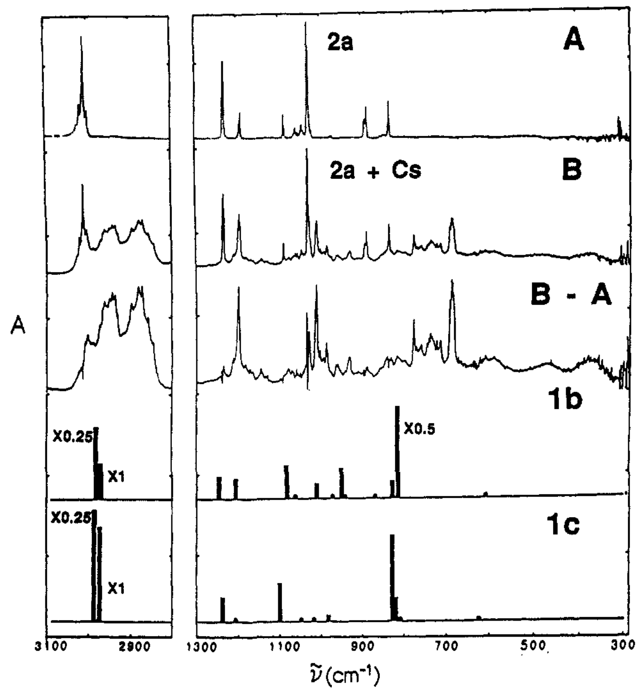
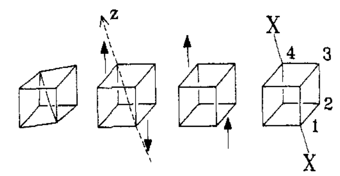


Figure 1. IR spectra in Ar at 12 K (top) and calculated, scaled by 10% (bottom). No significant IR absorption was observed outside the region shown.

Scheme I



1a 1b 1c 2 a X=I b X=Br

Codeposition of argon with 1,4-diiodocubane (**2a**)[11] to yield **1** (Scheme I) and K or Cs vapor, or 1,4-dibromocubane (**2b**)[12] and Cs vapor, on a cold CsI window yielded matrices colored by excess metal. IR showed much unreacted **2** and a series of bands (Figure 1) whose relative intensities and frequencies agreed (±5 cm^{-1}) in the three sets of experiments, suggesting that they belong to a single species **X**, different from authentic samples of cubane,[13] iodocubane,[14] and bromocubane[15] and containing neither a halogen nor a metal atom. The low C-H stretching frequencies fit expectations for hyperconjugating H-C-C•[16] or H-C-C⁻.[17]

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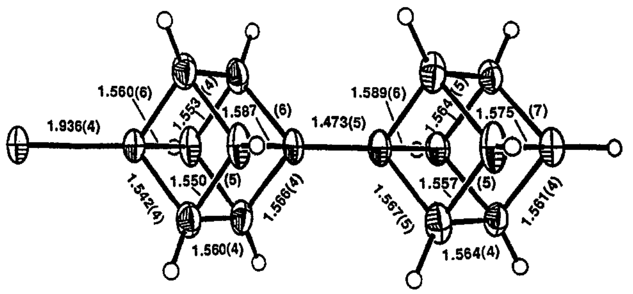


Figure 2. X-ray single-crystal structure of 3.[25] All endocyclic CCC valence angles are within 1° of 90°. The central CC bonds are perfectly staggered.

UV-visible irradiation has no effect, suggesting that **X** is not a free anion or dianion. ESR showed only metal peaks. Under identical conditions, strong ESR was obtained from radicals formed from Cs vapor with $Br(CH_2)_4Br$ and 1-bromoadamantane.

At ~40 K, all peaks associated with **X** disappear simultaneously, and cubane was detected as a new product by IR and subsequent GC–MS.

The earlier in the gas stream **2** and the metal vapor were mixed before deposition, the weaker the IR bands of **X** became. IR bands of cubane and traces of monohalocubanes appeared instead, until, under conditions previously used for [2.2.1]- and [2.1.1]propellanes,[3,4] only cubane was observed in the matrix IR spectrum and by photoelectron spectroscopy. Gradual replacement of halogens by hydrogens in dihalides[2-4] has been attributed[2] to hydrogen abstraction by initial radical products, with the dehydrogenation products sticking to the walls.

These results argue against anion, dianion, radical, radical anion, or triplet biradical structures and show that **X**, although diamagnetic, is a good hydrogen abstractor. The singlet 1,4-biradical structure **1b** appears highly probable.

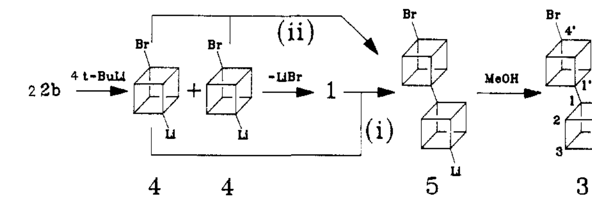
It agrees with ab initio 6-31G* calculations, which predict optimized **1b** (one-pair GVB,[18] R_{14} = 2.629 Å, cf. cubane, RHF, 2.700 Å, experimental[19] 2.683 Å) to lie 10.5 kcal/mol (11.1 including zero-point energy, ZPE) below optimized **1c** (ROHF, R_{14} = 2.581 Å). The relative phase of the singly occupied orbitals at C_1 and C_4 is antibonding. The large stabilization of their antisymmetric over their symmetric combination, responsible for the state order, is not due to ordinary through-bond coupling[20] but is understood readily when **1** is assembled from two C atoms and a "Moebius"[21] benzene sextuply twisted along its CH–CH bonds until they occupy positions appropriate for **1b**. The C_1–C_4 interaction is reflected in computed bond energies (ZPE included): C–H in cubane, 83.8 kcal/mol (RHF, ROHF); C_4–H in 1-cubyl, 75.4 kcal/mol (ROHF, one-pair GVB); ΔH (0 K) = 64.5 kcal/mol for cubane + C_2H_6 → **1b** + $2CH_4$ (RHF, one-pair GVB).

Configuration interaction[22] without further geometry optimization increased the **1b**–**1c** gap to 12.1 kcal/mol (12.7 using the ROHF–GVB ZPE). No local minimum was found at the "squashed" geometries of **1a** at which the symmetric orbital combination is lower: the stabilization by the central bond is more than compensated by the additional strain imposed on the other C–C bonds.[23]

Further evidence for the assignment of **X** as 1,4-cubadiyl is provided by the IR spectrum calculated for **1b** (GVB) and **1c** (ROHF), allowing for the known[24] difficulty in the calculation of IR intensities (Figure 1).

1b is probably also produced as a transient in solution. The reaction of **2b** with 2 equiv of t-BuLi in THF at −78 °C yielded 20% of 4-bromobicubyl (**3**)[25,26] (Figure 2, ^1H NMR fully analyzed by simulation, ^{13}C NMR fully assigned by HETCOR). The 1.473 (5) Å exocyclic C–C bond length has good precedent.[27]

Scheme II



Two likely paths to **3** are (i) loss of LiBr from 1-bromo-4-lithiocubane (**4**) to yield **1** and subsequent fast addition of **4** (cf. 1,4-dihalonorbornanes[28] and 1,2-dihalocubanes[29]) and (ii) direct coupling of two molecules of **4** (Scheme II). Under these conditions, 1-bromocubane fails to couple with 1-lithiocubane, and it is likely that path i is followed.

In summary, 1,4-dehydrocubane most likely has been observed in argon matrix and probably also produced in solution. It is a ground-state singlet 1,4-biradical and does not contain a body-diagonal bond.

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Registry No. 1, 277-10-1; **1b**, 124225-34-9; **2a**, 97229-08-8; **2b**, 59346-70-2; **3**, 124225-52-1; H_2, 1333-74-0; K, 7440-09-7; Cs, 7440-46-2; 1-cubyl, 67151-55-7; 1-bromocubane, 59346-69-9.

Supplementary Material Available: Experimental procedures, full details of the X-ray experiment, atomic positional and thermal parameters, bond lengths and angles, a thermal ellipsoid plot showing the atom-labeling scheme, a crystal packing diagram, and a space-filling representation of **3** (14 pages); a listing of observed and calculated structure factor amplitudes for **3** (12 pages). Ordering information is given on any current masthead page.

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(26) Mp: 150–152 °C. 500-MHz NMR in $CDCl_3$: ^1H, 3.87 ("d", $J_{2'3'} = J_{3'4'}$ = 5.0 Hz, $J_{2'4'} = J_{2'6'}$ = 2.0 Hz, $J_{2'7'}$ = −0.6 Hz, $J_{3'5'}$ = 2.7 Hz, 6 H, 2'-H, 3-H', 4'-H, 5'-H, 6'-H), 3.94 (m, J_{23} = 5.0 Hz, J_{26} = 2.2 Hz, J_{27} = −0.6 Hz, 3 H, 2-H, 6-H, 8-H), 4.04 (m, 1 H, 4'-H), 4.13 (m, J_{35} = 2.4 Hz, 3 H, 3-H, 5-H, 7-H); ^{13}C, 44.2 (C-3', C-5', C-7'), 44.8 (C-2, C-6, C-8), 46.3 (C-2', C-6', C-8'), 49.4 (C-4'), 54.1 (C-3, C-5, C-7), 57.1 (C-1), 58.6 (C-1'), 65.9 (C-4); IR (KBr) 2996, 2976, 2963, 1261, 1231, 1219, 1211, 1196, 1131, 1040, 921, 878, 834, 778, 756 cm^{-1}. MS: m/z (relative intensity) 204 (3), 202 (25), 189 (21), 178 (20), 165 (13), 152 (17), 139 (8), 127 (26), 115 (10), 102 (28), 89 (15), 77 (55), 63 (53), 51 (100).
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