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Molecular Orbital Theory of the Electronic Structure of Molecules. 39. Highly Unusual Structures of Electron-Deficient Carbon Compounds. Reversal of van't Hoff Stereochemistry in BBC Ring Systems[1]

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Abstract: It may be possible to violate all of van't Hoff's stereochemical rules! When two geminal hydrogens of methane, of ethylene, of allene, or of butatriene are replaced by a three-membered ring comprised of two BH groups, ab initio molecular orbital calculations indicate preference for anti-van't Hoff geometries: planar $(HB)_2CH_2$ (**6b**), perpendicular $(HB)_2C{=}CH_2$ (**7b**), planar $(HB)_2C{=}C{=}CH_2$ (**8b**), and perpendicular $(HB)_2C{=}C{=}C{=}CH_2$ (**9b**). These forms are estimated to be 15–20 kcal/mol more stable than the van't Hoff alternatives, **6a–9a.** The van't Hoff forms (**6a–9a**) exhibit classical Lewis two-center-two-electron bonding, with six σ electrons for the three diboracyclopropane ring bonds. In the anti-van't Hoff forms (**6b–9b**), the same rings have only four σ electrons; the two remaining electrons occupy an aromatic, cyclopropenium-ion-like π orbital. The geometrical consequences are shortening of the BB bonds and widening of the HBB angles in **6b–9b** over **6a–9a**, and, most particularly, retention of the exocyclic $C_1{=}C_2$ double bonds in the anti-van't Hoff forms (**7b–9b**). Both the perpendicular ethylene **7b** and its less stable planar isomer **7a** are found to be local minima, with a rotation barrier between them. Triplet forms of **6–9** do not appear to be competitive in energy with the singlets. Prospects for the experimental verification of these predictions are analyzed. Isolobal transition metal analogues may be best suited for this purpose.

Introduction

By linking carbon-based tetrahedra edge to edge, van't Hoff deduced in 1875 that the basic shapes of the cumulenes (**1**) should vary periodically.[3] When the number of double bonds, n, is odd, planarity (D_{2h} symmetry) is preferred, but perpendicular arrangements (D_{2d}) are favored when n is even. Methane (T_d), **1** with $n = 0$, can be considered to be the first member of this perpendicular series. These were remarkable predictions! At the time, neither allene (**1**, $n = 2$) nor any of its derivatives were known, and 60 years passed before van't Hoff's speculations concerning its stereochemistry were verified.[4] With butatriene (**1**, $n = 3$), an additional 24 years were required,[5] and the ground-state geometry of a pentatetraene was first established experimentally in 1976.[6] The rotational barrier in ethylene (**1**, $n = 1$) (65 kcal/mol) was determined in 1955,[7] but those for allene (~48 kcal/mol),[8] butatriene (~34 kcal/mol),[9,10] and the higher cumulenes only are of recent date.[10]

$$H_2C({=}C)_nH_2$$

1

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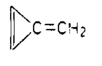
Table I. Molecular Equilibrium Geometries of Compounds **6–9**[a]

			optimization	
molecule	conformation[b]	parameter	STO-3G	4-31G
diboracyclopropane	perpendicular (**6a**)	r(B-B)	1.607	1.662
		r(B-C)	1.538	1.560
		r(B-H)	1.154	1.154[c]
		r(C-H)	1.083	1.083[c]
		∠(HBB)	158.5	160.0
		∠(HCH)	110.3	109.1
	planar (**6b**)	r(B-B)	1.437	1.490
		r(B-C)	1.547	1.593
		r(B-H)	1.146	1.146[c]
		r(C-H)	1.082	1.082[c]
		∠(HBB)	174.0	174.8
		∠(HCH)	106.4	107.6
2,3-diboramethylenecyclopropane	planar (**7a**)	r(B-B)	1.605	1.672
		r(B-C$_1$)	1.493	1.524
		r(C$_1$-C$_2$)	1.333	1.332
		r(B-H)	1.152	1.152[c]
		r(C$_2$-H)	1.093	1.093[c]
		∠(HBB)	158.4	159.5
		∠(HC$_2$H)	113.9	115.1
	perpendicular (**7b**)	r(B-B)	1.464	1.511
		r(B-C$_1$)	1.489	1.554
		r(C$_1$-C$_2$)	1.321	1.311
		r(B-H)	1.149	1.149[c]
		r(C$_2$-H)	1.095	1.095[c]
		∠(HBB)	172.0	173.7
		∠(HC$_2$H)	114.3	115.5
2,3-diboraethenylidenecyclopropane	perpendicular (**8a**)	r(B-B)	1.587	
		r(B-C$_1$)	1.488	
		r(C$_1$-C$_2$)	1.309	
		r(C$_2$-C$_3$)	1.291	
		r(B-H)	1.151	
		r(C$_3$-H)	1.082	
		∠(HBB)	159.8	
		∠(HC$_3$H)	117.5	
	planar (**8b**)	r(B-B)	1.472	
		r(B-C$_1$)	1.485	
		r(C$_1$-C$_2$)	1.297	
		r(C$_2$-C$_3$)	1.295	
		r(B-H)	1.149	
		r(C$_3$-H)	1.083	
		∠(HBB)	170.0	
		∠(HC$_3$H)	118.0	
2,3-diboraallenylidenecyclopropane	planar (**9a**)	r(B-B)	1.585	
		r(B-C$_1$)	1.485	
		r(C$_1$-C$_2$)	1.320	
		r(C$_2$-C$_3$)	1.253	
		r(C$_3$-C$_4$)	1.304	
		r(B-H)	1.151	
		r(C$_4$-H)	1.089	
		∠(HBB)	159.7	
		∠(HC$_4$H)	115.4	
	perpendicular (**9b**)	r(B-B)	1.483	
		r(B-C$_1$)	1.485	
		r(C$_1$-C$_2$)	1.306	
		r(C$_2$-C$_3$)	1.260	
		r(C$_3$-C$_4$)	1.299	
		r(B-H)	1.149	
		r(C$_4$-H)	1.091	
		∠(HBB)	169.4	
		∠(HC$_4$H)	115.7	

[a] Distances in ångströms, angles in degrees. In all cases, C_{2v} symmetry was assumed. [b] Refers to conformation around the terminal carbon atom; see text. [c] Not reoptimized; STO-3G values assumed.

Nevertheless, the general correctness of the van't Hoff cumulene rule has never been seriously questioned. All known cumulenes behave according to expectations. For example, the presence of the cyclopropene moieties in **2** and in **3** should not change matters; e.g., one can safely predict **2** to be planar and **3** to be perpendicular.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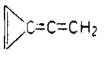
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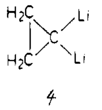
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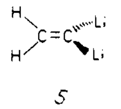
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Can the van't Hoff rules be violated fundamentally? Our research suggests that such possibilities exist. Thus, 1,1-di-

Table II. Absolute and Relative Energies of **6–9**[a]

molecule	conformation	STO-3G energy	rel *E*	4-31G energy	rel *E*	6-31G* energy	rel *E*	MP2/4-31G energy	rel *E*
				A. STO-3G Geometries					
diboracyclopropane	**6a**	−88.347 57	0.0	−89.315 88	0.0	−89.445 31	2.0	−89.501 50	11.4
	6b	−88.323 54	15.1	−89.311 67	2.6	−89.448 45	0.0	−89.519 66	0.0
2,3-diboramethylenecyclopropane	**7a**	−125.712 51	0.0	−127.106 50	0.7	−127.290 99	3.3	−127.378 99	15.1
	7b	−125.711 27	0.8	−127.107 54	0.0	−127.296 26	0.0	−127.403 02	0.0
2,3-diboraethenylidenecyclopropane	**8a**	−163.082 21	1.2	−164.902 30	1.9			−165.264 33	11.6
	8b	−163.084 16	0.0	−164.905 28	0.0			−165.282 82	0.0
2,3-diboraallenylidenecyclopropane	**9a**	−200.434 55	1.1	−202.675 77	1.6				
	9b	−200.436 25	0.0	−202.678 25	0.0				
				B. 4-31G Geometries					
diboracyclopropane	**6a**			−89.317 61	0.0	−89.447 07	2.5	−89.503 90	13.3
	6b			−89.315 20	1.5	−89.451 04	0.0	−89.525 03	0.0
2,3-diboramethylenecyclopropane	**7a**			−127.109 11	2.2	−127.293 52	4.2	−127.382 77	17.4
	7b			−127.112 58	0.0	−127.300 26	0.0	−127.410 53	0.0

[a] Absolute energies in hartrees (au's); relative energies in kcal/mol.

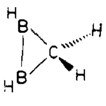
Table III. Net Charges in p Orbitals Perpendicular to (π) and in (Y) the Ring Plane, STO-3G[a]

molecule	$q_B{}^{\pi}$	$q_B{}^{Y}$	$q_{C_1}{}^{\pi}$	$q_{C_1}{}^{Y}$	$q_{C_2}{}^{\pi}$	$q_{C_2}{}^{Y}$	$q_{C_3}{}^{\pi}$	$q_{C_3}{}^{Y}$	$q_{C_4}{}^{\pi}$	$q_{C_4}{}^{Y}$
6a	0.047	0.904	0.991	1.225						
6b	0.466	0.919	1.067	1.026						
7a	0.133	0.899	0.979	1.213	0.756	1.017				
7b	0.475	0.904	1.045	1.045	1.039	0.731				
8a	0.165	0.903	1.056	1.220	0.667	0.965	1.018	1.132		
8b	0.416	0.906	1.083	1.124	1.011	0.634	1.074	1.031		
9a	0.179	0.900	1.018	1.227	0.736	1.007	0.992	1.074	0.897	1.032
9b	0.431	0.904	1.076	1.103	1.055	0.701	1.014	1.016	1.040	0.882

[a] $q_A{}^{\pi}$ is the charge in the 2p orbital perpendicular to the molecular plane on atom A. $q_A{}^{Y}$ is the charge in the p orbital of atom A in the ring plane and parallel with the B–B bond.

lithiocyclopropane (**4**) is indicated by theoretical calculations to have a planar tetracoordinate carbon,[11] and 1,1-dilithioethylene (**5**) to be perpendicular.[12] Although we have interpreted the structures of **4** and **5** in terms of multicenter covalent bonding involving lithium, the possibility that predominant ionic character is involved cannot be dismissed.[13] We have now discovered computationally a simple boron-based three-membered ring substituent, where ionic bonding is much less likely, which induces *planarity* when substituted on methane (**6b**) and allene (**8b**) and *perpendicular arrangements* in ethylene (**7b**) and butatriene (**9b**). The functioning of this remarkable "anti-van't Hoff BBC ring" is the subject of the present paper.

van't Hoff forms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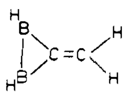
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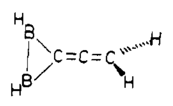
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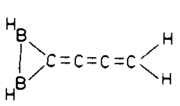
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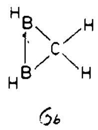
anti van't Hoff forms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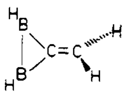
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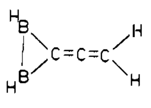
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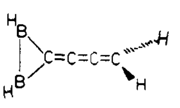

9b

Methods

Ab initio molecular orbital calculations were carried out on 6–9 using modified versions of the GAUSSIAN 70 series of programs.[14] Closed-shell electronic configurations were treated in the restricted Hartree–Fock (RHF) approximation specified by Roothaan[15a] and open-shell configurations in the unrestricted version (UHF) due to Pople and Nesbet.[15b] All geometrical variables of the perpendicular and planar conformations of **6–9** were optimized simultaneously assuming C_{2v} molecular symmetries (minimal STO-3G basis set)[16a] using programs based on the conjugate gradient scheme of Davidon, Fletcher, and Powell.[16b] Single-point calculations on the STO-3G optimized geometries with the split-valence 4-31G basis set (4-31G//STO-3G)[16a] were then performed. The sensitivities of the energies and of the geometries to this 4-31G basis were checked by reoptimizing all the geometrical variables of **6** and **7** (except the bond lengths to hydrogen, which were kept fixed at their STO-3G values). Modest changes (up to 0.07 Å) in the C–C, B–B, and C–B bond lengths were found, but very little alteration of the bond angles (Table I). The energies decreased modestly (1–3 kcal/mol). Single-point calculations with the 6-31G* basis set,[16c] which contains d-type polarization functions on carbon and boron, were performed on the optimized STO-3G and the optimized 4-31G structures of **6** and **7** (6-31G*//STO-3G and 6-31G*//4-31G). Finally, an estimate of correlation effects was obtained by the application of Møller–Plesset second-order perturbation theory[17] to the 4-31G wave functions of **6**, **7**, and **8** (MP2/4-31G). Absolute and relative energies are summarized in Table II. Net charges (Table III) and overlap populations ρ (Table IV) were calculated using the conventional Mulliken procedures;[18] for consistency, STO-3G values are given and are used in the discussion. STO-3G wave functions were used with Jorgensen's program[19] to prepare orbital diagrams shown in the figures; STO-3G orbital energies are given.

Geometries

The most remarkable geometrical feature is the length of the $C_1{=}C_2$ double bonds exocyclic to the rings. In the anti-van't Hoff forms (**7b–9b**) they are actually slightly (~0.01 Å) *shorter* than in the van't Hoff geometries (**7a–9a**)! This is

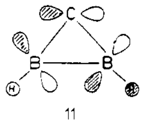
Table IV. Overlap Populations in **6–9**, STO-3G[a]

molecule	$\rho_{BB}{}^{\pi}$	$\rho_{BC_1}{}^{\pi}$	$\rho_{C_1C_2}{}^{\pi}$	$\rho_{C_2C_3}{}^{\pi}$	$\rho_{C_3C_4}{}^{\pi}$	$\rho_{BB}{}^{tot}$	$\rho_{BC_1}{}^{tot}$	$\rho_{C_1C_2}{}^{tot}$	$\rho_{C_2C_3}{}^{tot}$	$\rho_{C_3C_4}{}^{tot}$
6a	0.007	0.039				0.652	0.664			
6b	0.160	0.195				1.070	0.540			
7a	0.029	0.094	0.315			0.651	0.731	1.109		
7b	0.156	0.210	0.032			0.993	0.629	1.135		
8a	0.038	0.112	0.298	0.053		0.693	0.721	1.145	1.254	
8b	0.131	0.193	0.105	0.375		0.943	0.647	1.187	1.237	
9a	0.042	0.116	0.270	0.142	0.353	0.694	0.728	1.108	1.404	1.218
9b	0.137	0.195	0.094	0.394	0.034	0.945	0.654	1.154	1.378	1.227

[a] $\rho_{AB}{}^{\pi}$ is the Mulliken overlap population between two 2p orbitals centered on A and B and perpendicular to the ring plane; $\rho_{AB}{}^{tot}$ is the total overlap population between A and B.

consistent with the overlap populations, $\rho_{C_1C_2}{}^{tot}$, in Table IV, which are actually larger for **7b–9b**. The marked C–C lengthening in going from planar (1.33 Å) to perpendicular (1.48 Å) ethylene (**10**)[12] is not found. Two pronounced and systematic geometrical changes, characteristic of the bonding in all planar and all perpendicular conformations, occur in going from van't Hoff (**6a–9a**) to anti-van't Hoff (**6b–9b**) forms: the B–B bond lengths become considerably shorter (0.10–0.17 Å) and the HBB angles become much larger (10–15°). Since the differences in electronic structure between van't Hoff and anti-van't Hoff forms primarily involve the diboracyclopropane rings, the other geometrical parameters show much smaller differences between **6a–9a** and **6b–9b**.

The van't Hoff forms (**6a–9a**) have classical Lewis structures, rather adequately represented by two-center-two-electron bonds (details will be discussed below). Six electrons are involved in bonding the σ framework of the diboracyclopropane rings. Both of the familiar Walsh orbitals, shown schematically in **11** and **12**, are occupied (omitting the substituents on carbon and their corresponding orbitals).



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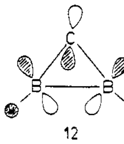

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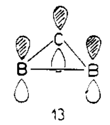

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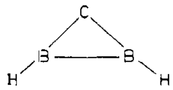
The anti-van't Hoff forms (**6b–9b**) have a different ring orbital occupancy with only four σ but two π electrons. The antisymmetric Walsh orbital **11** is no longer utilized; instead the aromatic π orbital **13** is occupied. (More elegant depictions of orbitals **11–13** for the actual systems, **6** and **7**, are given in Figures 1 and 2, respectively, and are discussed below). Cyclopropenium-ion-like orbital **13** is the key element governing the stability of the anti-van't Hoff forms: **13** is both BB and BC bonding. In **6b–9b**, **13** replaces **11**, which is BC bonding but BB antibonding. Consequently, in going from 6a–9a to 6b–9b the BC bond lengths are largely unaltered, but the BB bonds become much shorter. Likewise, **13** has no effect on the HBB angles (the hydrogens are in the nodal plane), but **11** contributes to the narrowing of the HBB angles. In **6b–9b**, **11** is not occupied and the HBB angles widen. Symbols **14** and **15** depict the structural and bonding differences in the van't Hoff and anti-van't Hoff systems. The dotted lines in **15** represent partial σ bonds, and the circle designates the aromatic two-electron-three-center π bond. We now turn to a more detailed discussion of the structures and bonding of individual species.



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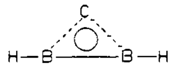

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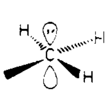
The orbitals of the two diboracyclopropane rotamers, **6a** and **6b**, are shown in Figure 1.[19] In both cases, the two highest occupied orbitals concern us in particular. These can be constructed from CH_2 and B_2H_2 fragments, each contributing two electrons to the eventual bonding. The familiar frontier orbitals of these fragments can be imagined to interact to form the two new carbon–boron bonds. Linear HB═BH offers degenerate π and degenerate π^* orbitals. The sp^2 orbital extending from the CH_2 group[19] interacts with the in-plane π B_2H_2 orbital nearly as well in **6a** as in **6b**; the resulting Walsh ($6a_1$) orbitals (Figure 1), like the other orbitals of a_1 symmetry, are similar in both geometries.

In contrast, the orbitals formed from interaction with the p CH_2 orbital are quite different in **6a** and **6b** and govern the bond length and bond angles calculated. In **6a**, this interaction is with the in-plane π^* B_2H_2 orbital. The resulting $3b_2$ Walsh MO has *antibonding* B–B character (Figure 1). To increase BH overlap, the BH hydrogens bend outward, away from carbon. In **6a**, <BBH = 160.0° (4-31G). In **6b**, the p CH_2 orbital interacts with the perpendicular π B_2H_2 orbital; the $2b_1$ LUMO and the fully bonding aromatic $1b_1$ π orbitals result (Figure 1). Bending of the BH hydrogens is not involved, and the linear HBBH arrangement is largely retained. In **6b**, <BBH = 174.8° (4-31G). This change in hybridization at B increases the 2s character of the B–H bonds; their lengths are reduced by almost 0.01 Å in the planar rotamer (1.154 Å in **6a** vs. 1.146 Å in **6b**, STO-3G). The C–H bond lengths are virtually identical in the two conformations, and the HCH angles change very little.

In **6b**, two electrons occupy a π ($1b_1$) orbital delocalized over three centers. The BBC ring thus acquires strong aromatic character (**13**). The ~0.5e residing in each boron $2p(\pi)$ orbital strongly enhances the π as well as the total bonding ($\rho_{BB}{}^{\pi}$ = 0.16; $\rho_{BB}{}^{tot}$ = 1.07 in **6b**, 0.65 in **6a**) and drastically shortens the boron–boron bond lengths, from 1.662 Å in **6a** to 1.409 Å in **6b** (4-31G). The C–B bonds are effectively single but have partial σ and partial π character (symbolized by **15**); only a slight increase in C–B bond length in **6b** occurs as compared to **6a**. In **6a**, as in cyclopropane, the three-membered ring bonds are "bent"; both the BC (1.538 Å) and the BB (1.607 Å) bond lengths are shorter than the standard values, 1.57 and 1.64 Å, respectively.[20] Hyperconjugation involving the π_{CH_2} orbital, discernible in the $2b_1$ (LUMO) orbitals of **6a** (Figure 1), leads to a small population (q = 0.05 e) in the out-of-plane boron 2p orbitals and slight π-bonding character in the BBC ring ($\rho_{BB}{}^{\pi}$ = 0.01).

Another description may help to explain the unusual stability of the planar tetracoordinate carbon species, **6b**. Planar methane has a lone pair of electrons in a p orbital (**16**); only six σ electrons are available to bind the four hydrogens.[11] In **6b**, the delocalization of this lone pair into the two boron p orbitals (**17**) provides great aromatic stabilization. The defi-



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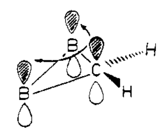

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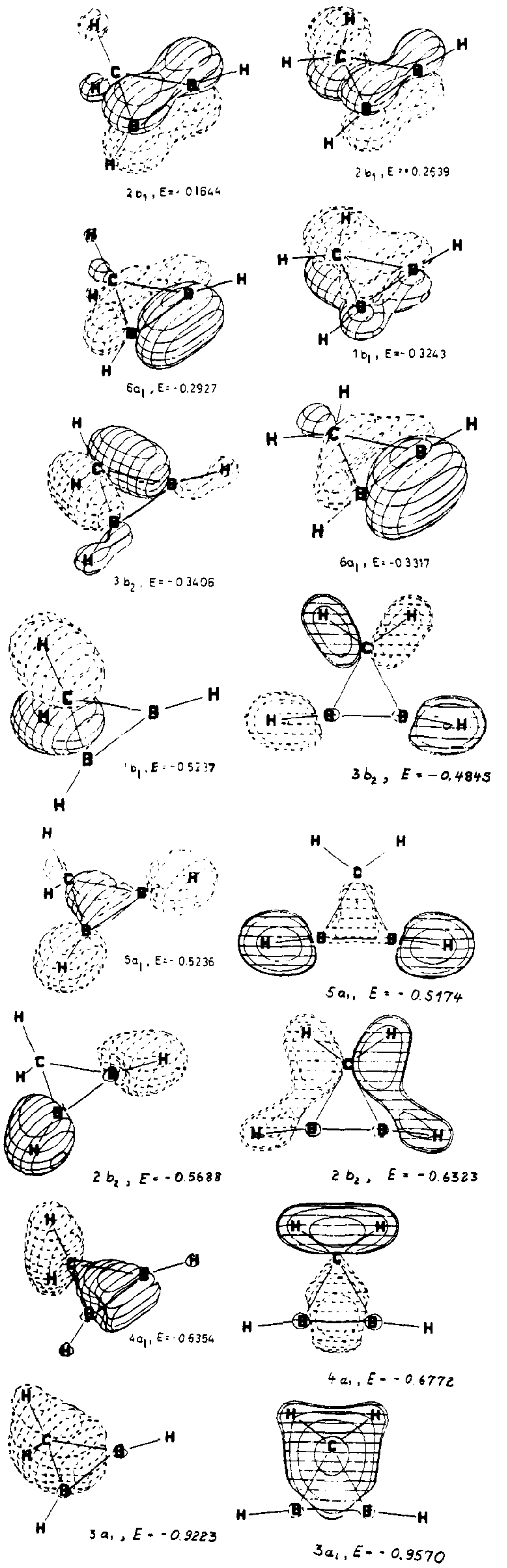


Figure 1. Molecular orbitals of **6a** (left side) and of **6b** (right side). The valence orbitals and the LUMOs ($2b_1$ in both cases) are shown. The MOs of **6a** closely resemble those of cyclopropene.[19] In **6b**, a Walsh cyclopropane MO (corresponding to $3b_2$ of **6a**) does *not* appear; it lies above the $2b_1$ orbital in energy and has been replaced by the $1b_1$ cyclopropenium-like orbital.

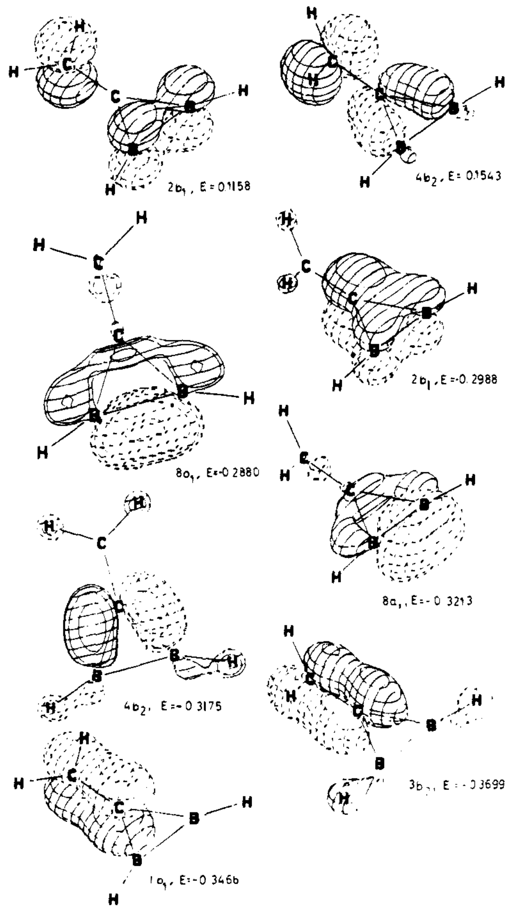


Figure 2. Molecular orbitals of **7b** (right side) and of **7a** (left side). The three occupied MOs of highest energy as well as the LUMOs are shown.[19] Note that the C=C double bond π orbital is one of the lower orbitals in both **7a** and **7b** ($1b_1$ and $3b_2$, respectively) and that the cyclopropenium-like $2b_1$ orbital has replaced one of the three-membered ring Walsh orbitals in **7b**.

ciency in σ electrons remains in **6b**. Since the ring orbitals are higher in energy than the CH orbitals, this deficiency now involves the three-membered ring, rather than the hydrogens attached to carbon. Thus, the $3b_2$ orbital in **6b** has largely CH (and BH) bonding character. In classical terms, we might say that some of the "strain" of the three-membered ring has been relieved by transforming a partially antibonding Walsh σ orbital (**11**) into a fully bonding π orbital (**13**).

The basic pattern describing **6a** can be applied to all the remaining van't Hoff structures (**7a**, **8a**, and **9a**). The two carbon–boron σ bonds arise from the interaction between a B_2H_2 fragment and a carbene-like ene or polyene fragment. Similarly, the pattern from the planar **6b** applies to the anti-van't Hoff structures **7b**, **8b**, and **9b**; the appropriate fragments form the two new MOs (one σ and one π) which hold the "complex" together. Figure 2 compares the molecular orbitals of **7a** and **7b**.

The olefinic fragment in 2,3-diboramethylenecyclopropane (**7**) is ethenylidene, :C=CH$_2$. In **7a** the two π C=C electrons are delocalized into the boron 2p orbitals ($q_B{}^\pi = 0.13$, $\rho_{BB}{}^\pi = 0.03$) and the $1b_1$ orbital (Figure 2) results. This shortens the carbon–boron bond (1.524 Å in **7a** vs. 1.560 Å in **6a**, 4-31G), but the boron–boron bond has nearly the same length as in **6a** (1.672 vs. 1.662 Å). The stabilization of the ring arises partly at the expense of the carbon–carbon double bond, which lengthens to 1.332 Å, longer than the value (1.316 Å) calculated in ethylene itself (4-31G).[21] The perpendicular rotamer, **7b**, shows the characteristic reduction in the boron–boron length (r(B–B) = 1.464 Å, $\rho_{BB}{}^\pi = 0.16$, $q_B{}^\pi = 0.48$) and the widening of the HBB angles. Whereas in perpendicular ethylene the π bond is broken (r(C–C) = 1.488 Å)[12,21] and one electron resides in each of the orthogonal 2p orbitals, in perpendicular 2,3-diboramethylenecyclopropane (**7b**) the double bond is fully intact. This is shown visually by the $3b_2$ orbital of **7b** in Figure 2. The π bond in ethenylidene now in the heavy atom plane has the correct symmetry to interact with the in-plane LUMO of the B_2H_2 fragment. Electron donation into the σ system of the BBC ring is thus possible, primarily to the B-C bonds. No lengthening of the C=C bond (1.311 Å, 4-31G) compared to ethylene is observed; r(C=C) also is shorter than in **7a**. The boron-carbon distance is essentially unaffected as the σ component is weakened compared to **7a** but the π component is strengthened. C-C bonding in **7b** is also strengthened through hyperconjugation with the CH_2 group (the antibonding combination is shown in the $2b_1$ orbital, Figure 2).

The two π systems in unsubstituted D_{2d} allene are orthogonal and do not interact. Substituents can have only the relatively small influence expected from attachment to a double bond.[22] In the perpendicular 2,3-diboraethenylidenecyclopropane (**8a**), one of the π systems is concentrated between C_2 and C_3 (Table III), but the other π system is delocalized onto the boron atoms. This delocalization is somewhat more effective than in **7a** ($q_B{}^\pi = 0.17$, $\rho_{BB}{}^\pi = 0.04$), partly due to hyperconjugative donation from the CH_2 group. Consequently, the B-B bond is shorter than in **7a** by 0.02 Å and the C_1-C_2 bond in **8a** is slightly longer than the C_2-C_3 bond (1.309 vs. 1.291 Å, STO-3G). In the planar D_{2h} conformation of allene the three carbon 2p orbitals form an extended allyl-like π system which may hold two, three, or four electrons.[22-24] The remaining 2p orbital at C_2 is orthogonal to this system and may correspondingly be filled, singly occupied, or empty. The rotation in allene itself apparently involves an open-shell singlet state with three π electrons.[23,24] However, the four π electron allyl anion-like state, although lying about 20 kcal/mol higher in energy in allene itself,[23] is much more sensitive to the influence of stabilizing substituents.[22] Thus, planar 2,3-diboraethenylidenecyclopropane (**8b**) has four π electrons delocalized over all five p(π) orbitals. The electronic demands of the allene σ system are satisfied through strong hyperconjugation with the B-C bonds whose high p character and modest polarization toward carbon B^+-C^- give them excellent electron-donating ability. The population in the in-plane 2p orbital on C_2 is 0.63e. The C_1=C_2 bond and especially the B—B bond shorten in **8b** as compared to **8a**, while the B—C bond length remains constant. The total overlap population between C_2 and C_3 changes insignificantly from 1.25 in **8a** to 1.24 in **8b**, so the C_1=C_2 double bond remains intact with a length of 1.295 Å (STO-3G). Both 1,1,3,3-tetralithioallene[25b] and 1,1-dilithioallene[25h] are also calculated to be more stable planar than perpendicular if standard bond angles are assumed; however, lithium-bridged structures are indicated to be much more stable in both instances.

Planar 2,3-diboraallenylidenecyclopropane (**9a**) has four π electrons in a six-center system; two electrons in the in-plane π system form a separate π bond between C_2 and C_3. The C_2=C_3 bond length (1.253 Å) is intermediate between that of a double and of a triple bond and is considerably shorter than C_3=C_4 (1.304 Å) and C_1=C_2 (1.320 Å, STO-3G). The BBC ring dimensions are quite similar to those of **8a**, as are the charges and the overlap populations (Tables III and IV). In the perpendicular conformation **9b**, the C_2=C_3 π electrons delocalize into the available orbital on C_4. Simultaneously, electrons are drawn hyperconjugatively from the B-C bonds. There are effectively 2.6e in this three-center system (Table III). C_1=C_2 and C_3=C_4 shorten slightly while C_2=C_3 lengthens upon rotation from **9a** to **9b**.

Relative Energies

At sufficiently high calculational levels (Table II) all anti-van't Hoff conformations, **6b**-**9b**, are more stable than **6a**-**9a**! An earlier, partial optimization of the two diboracyclopropane conformers, assuming fixed HBB angles, gave energy preferences of 34.2 (STO-3G) and 19.5 kcal/mol (4-31G//STO-3G) for **6a**.[11] Complete optimization reduces this separation to 15.1 (STO-3G) and to only 1.5 kcal/mol (4-31G//4-31G). Much of this added stabilization of **6b** comes from the widening of the HBB angles in **6b**, not suspected in the earlier study. With the inclusion of d functions (6-31G*//4-31G) or with electron correlation (MP2/4-31G//4-31G) planar **6b** is favored over **6a** by 2.5 and 13.3 kcal/mol, respectively (Table II). If we combine the correlation energy difference with the best Hartree-Fock result on the best geometry, a preference for **6b** of 18-19 kcal/mol is indicated! From an energy difference between T_d and D_{4h} methane of about 150 or 141 kcal/mol (4-31G//STO-3G) for cyclopropane with one planar CH_2 group vs. normal cyclopropane,[11] this situation represents quite a change!

At the minimal basis set level **7a** is preferred over **7b** by 0.8 kcal/mol, but at 4-31G//STO-3G the perpendicular conformation **7b** is more stable by 0.7 kcal/mol; 4-31G optimization increases the value to 2.2 kcal/mol. This energy difference increases to 4.2 kcal/mol at 6-31G*//4-31G and to 17.4 kcal/mol with the inclusion of correlation (MP2/4-31G//4-31G). Instead of the 65 kcal/mol barrier of ethylene,[6,12] with the planar form being preferred, we now have an olefin indicated to prefer the perpendicular **7b** over the planar **7a** conformation by some 19 kcal/mol if the results from the various levels are combined (4-31G geometries).

2,3-Diboraethenylidenecyclopropane (**8**) and 2,3-diboraallenylidenecyclopropane (**9**) prefer the anti-van't Hoff conformations at STO-3G by 1.2 and 1.1 kcal/mol, respectively. These preferences increase to 1.9 and 1.6 kcal/mol at 4-31G//STO-3G. Correlation again increases separation between the two rotamers of **8**, to 11.6 kcal/mol. Use of larger basis sets and higher level geometry optimizations should increase this difference. Although we have not been able to carry out such calculations on **9**, **9b** should be favored as much as **6b**, **7b**, and **8b**. We conclude that all anti-van't Hoff structures (**6b**-**9b**) are favored with respect to their "normal" rotamers (**6a**-**9a**), possibly by 15-20 kcal/mol.

Rotation Barriers

Both planar and perpendicular forms of 1,1-dilithioethylene were found to be minima (STO-3G) on the singlet rotational energy surface, but the barrier between them was quite small.[12] Similarly, the 2,3-diboramethylenecyclopropane conformations **7a** and **7b** both represent C_{2v} minima, at least at the STO-3G and 4-31G levels. The barriers to nonrigid rotation were calculated (Table VI) by employing twist angle grids of 15° and assuming C_2 symmetry; the geometries were optimized at each point (STO-3G) and subjected to single-point 4-31G calculations. The barrier separating **7a** and **7b** (roughly at a 45° twist angle) lies 4.4 kcal/mol above the most stable conformation (**7b**) (4-31G//STO-3G), but the details of the potential energy surface are expected to change at higher theoretical levels. The rotational potential surface connecting **6a** and **6b** was probed similarly, assuming C_2 symmetry. The results were method dependent (Table VI); it probably is unwise to come to any conclusions concerning the number of CB_2H_4 minima until further higher level calculations can be carried out.

Higher Spin States

The possibility of low-lying states of higher spin multiplicity was checked by calculating the two lowest triplet states of **6**-**9** at the UHF/STO-3G level using optimized STO-3G singlet geometries (Table V). Owing to the low-lying π MO concentrated on the boron atoms (note the smaller HOMO-LUMO

Table V. Relative Energies of the Lowest Lying Triplet States and the Expectation Values of S^2 [a]

molecule	state	lowest triplet energy	$\langle S^2 \rangle$ [b]
6a	$^3B_1$	36.9	2.021
6b	$^3A_1$	93.2	2.016
7a	$^3B_1$	9.5	2.153
7b	$^3A_2$	44.1	2.011
8a	$^3B_1$	19.3	2.432
8b	$^3A_1$	67.6	2.017
9a	$^3B_2$	−4.3	2.628
9b	$^3A_2$	15.7	2.163

[a] UHF/STO-3G energies in kcal/mol, relative to the STO-3G energies of the lowest singlets. Singlet geometries were employed. [b] Values of $\langle S^2 \rangle$ exceeding 2.000 indicate contamination by higher spin states.

Table VI. Variation of Energy with Rotation

twist angle,[a] deg	energy, au (STO-3G)[b]	rel *E*, kcal/mol	energy (4-31G)[b]	rel *E*, kcal/mol	energy (MP2/4-31G)[b]	rel *E*, kcal/mol
			A. Diboracyclopropane (**6**)			
0 (**6b**)	−88.323 54	15.1	−89.311 67	2.6	−89.519 66	0.0
15	−88.323 60	15.0	−89.310 92	3.1	−89.518 29	0.9
30	−88.324 21	14.7	−89.309 04	4.3	−89.514 04	3.5
45	−88.327 18	12.8	−89.307 67	5.2	−89.507 46	7.7
60	−88.334 71	8.1	−89.309 44	4.0	−89.502 07	11.0
75	−88.343 67	2.4	−89.313 65	1.4	−89.500 99	11.7
90 (**6a**)	−88.347 57	0.0	−89.315 88	0.0	−89.501 50	11.4
			B. 2,3-Diboramethylenecyclopropane (**7**)			
0 (**7a**)	−125.712 50	0.0	−127.106 50	0.7		
30	−125.708 10	2.8	−127.102 27	3.3		
45	−125.706 20	4.0	−127.100 55	4.4		
60	−125.707 83	2.9	−127.103 57	2.5		
75	−125.710 18	1.5	−127.105 89	1.0		
90 (**7b**)	−125.711 25	0.8	−127.107 54	0.0		

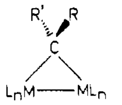
[a] Except for **6a**, **6b**, **7a**, and **7b**, C_2 symmetry assumed. [b] Optimized STO-3G structures.

splittings of **6a**–**9a** (Table VII)), all the van't Hoff conformations have by far the lowest energy triplet states. Only in **9a** was a triplet state energy indicated to be below a singlet. However, this triplet state is highly spin contaminated ($\langle S^2 \rangle$ = 2.628) from configurations of higher multiplicity. Since UHF generally artificially favors higher spin states through such spin contamination,[11,12,23,26] it seems likely that **6**–**9** all have singlet ground states. Higher level calculations with geometry optimization of the triplets are needed to substantiate this conclusion, but we did not pursue the matter further.

Prospects for Experimental Realization

After more than a century of van't Hoff stereochemistry,[3] our predictions that fundamental exceptions might be found stimulate interest in experimental verification. To the polylithio examples described earlier,[11,12,25] we now have added diboracyclopropane-based systems. Three-membered rings containing two borons and a carbon abound as part structures in the carboranes,[27] but are not known as isolated entities. However, no attempts to synthesize such systems have been reported, as far as we are aware. As in most theoretical work, the parent structures with hydrogen substituents were calculated. More suitable synthetic targets would have other groups designed to provide chemical stability or to facilitate preparation. Substituents on boron cannot be good π donors (like the halogens); our further calculations indicate that this will spoil the desired effect.[28] Alkyl or possibly aryl groups may be suitable. A study of the effects of substituents will be presented subsequently to help guide experimental work.[28]

It may be possible to realize anti-van't Hoff structures more easily in transition-metal complexes. A number of these are now known in which methylene,[29] substituted methylene (**18**),[29,30] and ethenylidene (**19**)[31] groups bridge two metals. All the known cases are coordinatively saturated, and the organic moieties adopt the classical stereochemistry.



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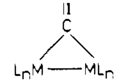

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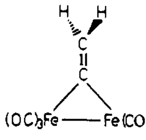
Wade has pointed out the analogies between transition-metal fragments and groups comprised of first-row elements and hydrogen.[32] Thus, $Fe(CO)_3$ and BH are "isolobal", to use Hoffmann's terminology.[33] Consequently, **20**, like **7b**, may prefer to have a perpendicular double bond. Indeed, model geometry EHT calculations indicate **20** to be somewhat more stable than **21**![34] **20** is not likely to be chemically stable, but other coordinatively unsaturated species (e.g., **22**)[34] should be more suitable for experimental study.

Table VII. Orbital Energies (au)

molecule	HOMO energy	LUMO energy	energy difference
	STO-3G//STO-3G		
6a	−0.2925	0.1645	0.4570
6b	−0.3243	0.2638	0.5881
7a	−0.2880	0.1158	0.4038
7b	−0.2988	0.1542	0.4530
8a	−0.2829	0.1157	0.3985
8b	−0.2697	0.1622	0.4319
9a	−0.2711	0.0791	0.3502
9b	−0.2564	0.0969	0.3533
	4-31G//STO-3G		
6a	−0.3435	0.0486	0.3921
6b	−0.3792	0.1344	0.5139
7a	−0.3441	0.0156	0.3597
7b	−0.3573	0.0632	0.4205
8a	−0.3436	0.0190	0.3626
8b	−0.3327	0.0738	0.4065
9a	−0.3337	−0.0129	0.3208
9b	−0.3219	0.0110	0.3329



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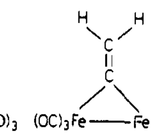

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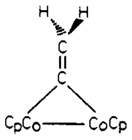

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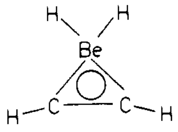
We have also investigated a number of species isoelectronic and isostructural with **6–9**; all prefer anti-van't Hoff geometries.[28] Examples include **23–27**.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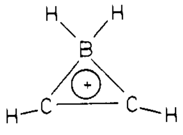
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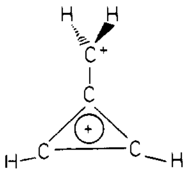
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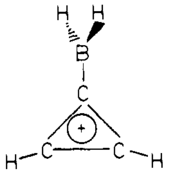
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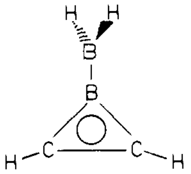
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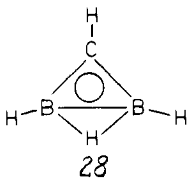
28

Complications are illustrated by **28**, an isomer of 6 with a three-center BHB bond, indicated to be 31.7 kcal/mol (4-31G//STO-3G) more stable than **6b**.[35] Although the structure of **28** is interesting, it does not possess a planar tetracoordinate carbon. In calculational studies on molecules not obeying classical bonding rules, it is difficult to ensure that the geometry with the global minimum energy has been located. If CB_2H_4 were to be synthesized, the structure might well be **28**, instead of **6b**.[36] However, this would not vitiate the principles developed in this paper. For example, the use of other substituents should avoid the complication of hydrogen bridging in **28**.

Conclusion

It should be possible to find many systems displaying anti-van't Hoff stereochemistry. A molecule containing a planar, tetracoordinate carbon is already known.[37]

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Determination of the β-Anomeric Configuration of Cytidine 5'-Monophospho-*N*-acetylneuraminic Acid by ^{13}C NMR Spectroscopy[1,2]

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Abstract: The anomeric configuration of the NeuAc residue in enzymically prepared cytidine 5'-monophospho-*N*-acetylneuraminic acid was established to be β on the basis of the heteronuclear vicinal coupling constant $^3J_{\mathrm{C1-H3ax}}$. For comparison the $^3J_{\mathrm{C1-H3}}$ values of a number of α and β *N*-acetylneuraminic acid derivatives have also been determined. The biochemical implication of this finding is discussed.

The biosynthesis of cytidine 5'-monophospho-*N*-acetylneuraminic acid (CMP-NeuAc) from CTP and NeuAc is catalyzed by the enzyme acylneuraminate cytidylyltransferase (EC 2.7.7.43):[4-7]

$$\text{CTP} + \text{NeuAc} \xrightarrow{\text{transferase}} \text{CMP-NeuAc} + \text{PP}_\text{i}$$

CMP-NeuAc is a key intermediate in the biosynthesis of glycoconjugates. The enzyme sialyltransferase (EC 2.4.99.1) transfers NeuAc residues from this donor molecule to oligosaccharides, glycoproteins, and glycolipids (in the following equation "R").

$$\text{CMP-NeuAc} + \text{glycosyl-R} \xrightarrow{\text{transferase}} \text{NeuAc}\alpha(2 \rightarrow x)\text{glycosyl-R} + \text{CMP}$$

(x = 3 or 6 in the case of a hexosyl unit and 8 or 9 in the case of a neuraminyl unit).

To investigate the mechanism of these enzymic reactions the anomeric configuration of CMP-NeuAc has to be known. In the literature ambiguity exists about this configuration. Comb et al.[8] proposed a β-glycosidic linkage on the basis of optical rotation measurements. However, circular dichroism measurements led Stone and Kolodny[9] to the suggestion that an α-glycosidic linkage should exist.

In this paper the determination of the anomeric configuration of CMP-NeuAc by single-resonance ^{13}C NMR spectroscopy is described. The coupling constant $^3J_{\mathrm{C1-H3ax}}$ is indicative of the anomeric configuration since its magnitude depends on the torsion angle between the coupled carbon and hydrogen atom (see Figure 1) according to a Karplus-type relation.[10-13]

Experimental Section

Synthesis of CMP-NeuAc. The incubation mixture (80 mL, pH 9) for the synthesis of CMP-NeuAc contained the following components: 0.8 mmol of NeuAc, 3.2 mmol of CTP (Boehringer, Mannheim), and 30 nkat enzyme preparation from frog liver.[14] The concentrations of Tris, Mg^{2+}, and mercaptoethanol were 0.4, 0.04, and 0.001 M, respectively. After 4 h of incubation at 37 °C the mixture was diluted tenfold with water and rinsed through a column of Dowex 2-X4, HCO_3^- form (0.8 L resin). After washing with 2 L of 1 mM ammonia the sialic acid derivatives were eluted by 3 L of a linear gradient from 0.01 to 2.0 M triethylammonium hydrogen carbonate buffer, pH 7.8. The fractions containing CMP-NeuAc[15] were pooled and lyophilized. The material was stored at −20 °C under NH_3 vapor. Thin layer chromatographic analysis of the product was carried out on cellulose plates using 95% ethanol-1 M ammonium acetate, pH 7.3 (7:3 v/v),[8] as solvent. The R_f value for CMP-NeuAc is 0.26 and for NeuAc 0.56.

Synthesis of Reference Compounds. NeuAc methyl ester β-methylglycoside (**2**) and the corresponding α anomer (**3**) were prepared according to Yu and Ledeen.[16] NeuAc α-methylglycoside (4) was obtained from **3** by saponification at 40 °C in D_2O, kept at pD ~11 with triethylamine. The reaction was followed by ^{1}H NMR analysis; after disappearance of the ester methyl signal at 3.88 ppm relative to sodium 2,2-dimethyl-2-silapentane-5-sulfonate the solution was lyophilized.

^{13}C NMR Spectroscopy. ^{13}C Fourier transform spectra were recorded in 12 mm o.d. sample tubes at 25.16 MHz on a Varian XL-100-15 spectrometer at 25 °C for compounds **1–4** and at ~15 °C for CMP-NeuAc. Samples of **1–4** were examined as neutral 0.7 M solutions in D_2O, and CMP-NeuAc as 0.3 M solutions in D_2O at pD ~8. Coupling constants were determined from the single-resonance ^{13}C spectra using 8192 data points over 250-Hz spectral width. The stability of CMP-NeuAc during the NMR experiments was checked by thin layer chromatography (see above).

Results and Discussion

^{13}C NMR spectra of CMP-NeuAc and the reference compounds β-NeuAc (**1**), NeuAc methyl ester β-methylglycoside (**2**), NeuAc methyl ester α-methylglycoside (**3**), and NeuAc α-methylglycoside (**4**) in D_2O were recorded under various conditions: (1) proton noise decoupled spectra for product control[17] and (2) single-resonance spectra of the carbonyl region (250-Hz spectral width) to determine the anomeric configuration. Chemical shifts and coupling constants of the carboxylate and *N*-acetyl carbonyl carbons are given in Table 1. The assignment of these resonances was made on the basis of the various coupling constants (see also Figures 2 and 3). The resonance of C1 in **1** and in CMP-NeuAc (Figure 3) is a

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