13: m/z (%) 238 (0.3, M^+), 207 (5, $M^+ - OCH_3$), 179 (2), 178 (7), 177 (9), 175 (1), 163 (5), 147 (20), 139 (5), 135 (4), 131 (11), 130 (26), 115 (10), 109 (18), 108 (100, anisole), 103 (9), 101 (17), 99 (17), 91 (10), 78 (16, anisole − CH_2O), 77 (9, 78 − H$^\bullet$),[35] 75 (23), 71 (12), 65 (8), 45 (10), 41 (8).

14: m/z (%) 238 (0.9, M^+), 207 (8, $M^+ - OCH_3$), 179 (2), 178 (8), 177 (9), 175 (1), 163 (5), 147 (20), 139 (5), 135 (4), 131 (11), 130 (29), 115 (9), 109 (18), 108 (100, anisole), 103 (9), 101 (16), 99 (20), 91 (10), 78 (15, anisole − CH_2O), 77 (9, 78 − H$^\bullet$),[35] 75 (23), 71 (13), 65 (8), 45 (10), 41 (8).

15: m/z (%) 260 (0.3, M^+), 259 (2, M^+ − H), 229 (21, $M^+ - CH_3O$), 197 (19), 168 (11), 140 (52), 139 (28), 137 (15), 125 (14), 109 (33), 101 (12), 99 (11), 97 (11), 75 (100), 45 (18), 41 (17).

16: m/z (%) 236 (0.4, M^+), 163 (2), 147 (3), 131 (3), 128 (1), 127 (6), 115 (3), 109 (9), 108 (100, anisole), 103 (5), 101 (5), 95 (4), 91 (5), 79 (3), 78 (11, anisole − CH_2O), 77 (5), 75 (3), 65 (5), 45 (5), 41 (4), 39 (4).

17: m/z (%) 236 (4, M^+), 172 (1), 163 (1), 147 (2), 146 (1), 131 (2), 129 (1), 128 (1), 127 (1), 117 (1), 115 (2), 109 (8), 108 (100, anisole), 103 (4), 101 (2), 97 (2), 95 (1), 93 (2), 91 (4), 79 (3), 78 (11, anisole − CH_2O), 77 (3), 75 (2), 65 (4), 45 (3), 41 (3), 39 (3).

^{13}C NMR data (C_6D_6, TMS, **15**: $C_6D_6 + CS_2$). **11**: 35.1, 37.5, 52.6, 52.7, 53.9, 55.4, 56.0, 69.3, 94.8, 105.7, 111.5, 128.8, 133.6. **12**: 35.5, 38.8, 50.2, 54.0, 54.2, 55.9, 56.2, 61.6, 89.0, 109.4, 111.0, 127.2, 134.0. **13**: 35.2, 35.5, 46.6, 53.5, 56.1, 57.0, 62.0, 89.2, 105.8, 107.6, 127.6, 133.0 (two C isochrone). **14**: 36.0, 40.3, 50.2, 51.6, 54.5, 56.5, 56.7, 58.0, 89.5, 106.2, 108.6, 127.1, 135.0. **15**: 39.1, 40.4, 53.8, 57.1, 105.8, 107.6. **16**: 37.3, 38.0, 42.1, 53.8, 53.9, 55.9, 56.1, 56.7, 67.9, 81.5, 85.9, 95.3, 130.8, 134.3. **17**: 35.4, 37.0, 37.3, 45.7, 51.1, 56.0, 56.4, 56.8, 57.4, 79.1, 79.2, 88.8, 127.4, 135.4.

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Registry No. **8**, 5143-07-7; **9**, 5143-08-8; **10**, 59415-72-4; **11**, 129215-89-0; **12**, 129263-09-8; **13**, 129263-11-2; **14**, 129263-12-3; **15**, 129215-91-4; **16**, 129215-90-3; **17**, 129263-10-1; DMF, 68-12-2; PhOMe, 100-66-3; MeI, 74-88-4; BaO, 1304-28-5; *cis*-1,4-dihydroxycyclopent-2-ene, 29783-26-4.

Through-Bond Interactions of β-Carbonyl and β-Imine Lone Pairs with Cationic 2p Orbital. Quantum Calculations on Bicyclo[2.2.2]oct-1-yl Cation and Derivatives[†]

Pierre-Alain Carrupt and Pierre Vogel*

Section de Chimie de l'Université, CH-1005 Lausanne, Switzerland

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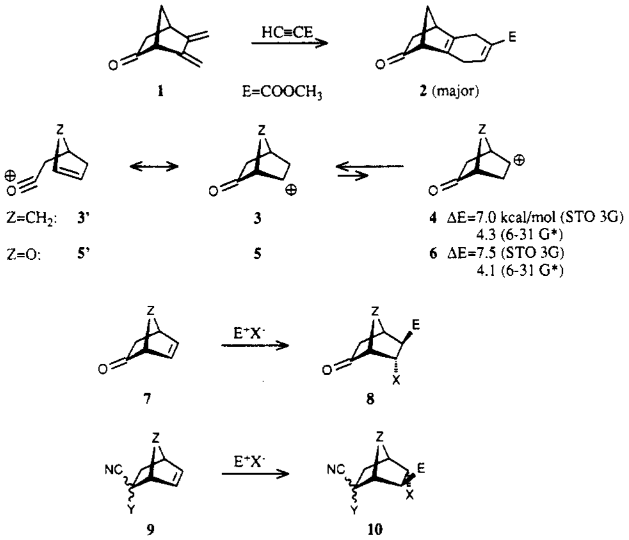
Semiempirical AM1 and ab initio STO 3G quantum calculations on bicyclo[2.2.2]oct-1-yl cation (**11**) and derivatives (**12–25**) substituted at C(2) or C(3) with electron-withdrawing groups such as Z = O, NH, CH_2, $C(CN)_2$ or X = CN and NO_2 suggested that the 3-oxobicyclo[2.2.2]oct-1-yl cation (**13**) and 3-(*E*)-iminobicyclo[2.2.2]oct-1-yl cation (**15**) are more stable than expected on the basis of the inductive effect of their oxo and imino substituents, respectively. This phenomenon has been attributed to favorable through-bond n(CO) ↔ σC(2),C(3) ↔ $p(C(1))^+$ and n((*E*)-NH=C) ↔ σC(2),C(3) ↔ $p(C(1))^+$ interactions. This electron-releasing effect of the imino substituents is less important in the 3-(*Z*)-iminobicyclo[2.2.2]oct-1-yl cation (**17**).

In a recent publication in this journal on the solvolysis of 3-oxobicyclo[2.2.2]oct-1-yl triflate and derivatives, Takeuchi and Yoshida[1] claimed to have discovered the first example of the through-bond interaction of the β-carbonyl lone pair with cationic p orbital. Already in 1978, we reported that 5,6-dimethylidenebicyclo[2.2.1]heptan-2-one (**1**) added to methyl propynoate with a relatively good "para" regioselectivity, giving **2** as major adduct.[2] The results were in agreement with predictions based on the FMO theory[3] which considers the HOMO(diene)-LUMO(dienophile) orbital interaction to control the regioselectivity of the cycloaddition.[2,4] The shape of the HOMO of **1** suggested the intervention of a through-bond interaction of type n(CO) ↔ σ(C(1),C(2)) ↔ π(C(5),C(6)) making the p atomic coefficients at C(6)=CH_2 significantly larger than those at C(5)=CH_2.[4,5] Semiempirical MO calculations, first,[6] and than ab initio MO calculations[7,8] predicted that the 6-oxobicyclo[2.2.1]hept-2-yl cations **3**, **5** are more stable than their 5-oxo isomers **4**, **6** due to favorable n(CO) ↔ σ(C(1),C(6)) ↔ $pC(2)^+$ interactions that render the carbonyl group electron-releasing in the former carbocations. These predictions were supported by the regioselectivity observed for the electrophilic additions of enones **7** and of their synthetic precursors **9** which led to adducts **8** and **10**, respectively,[9,10] under conditions of kinetic control. We also found that an acyl group has a



[†] Dedicated to Dr. Paul von Ragué Schleyer on the occasion of his 60th birthday.

(1) (a) Takeuchi, K.-I.; Yoshida, M. *J. Org. Chem.* **1989**, *54*, 3772–3773. (b) For earlier examples of heterolyses of 3-oxo-1-alkyl derivatives, see: Udding, A. C.; Wynberg, H.; Strating, J. *Tetrahedron Lett.* **1968**, 5719–5722. Banerjee, S.; Werstiuk, N. H. *Can. J. Chem.* **1976**, *54*, 678–684.

greater intrinsic (kinetic) migratory aptitude than an alkyl group in exothermic Wagner–Meerwein rearrangements.[8,11]

We report here further theoretical studies on the hypothesis of electron-releasing homoconjugated carbonyl group and we shall confirm the proposal of Takeuchi and Yoshida that in 3-oxobicyclo[2.2.2]oct-1-yl cation the destabilizing inductive effect of the carbonyl group is compensated by its electron-donating ability due to favorable through-bond n(CO) ↔ σC(2),C(3) ↔ pC(1)$^+$ interaction. Our approach is based on the comparison of the calculated hydride affinities and geometries in bicyclo[2.2.2]oct-1-yl cation **11** and its 2-oxo (**12**) and 3-oxo derivatives (**13**). Analogous analyses have been carried out also for bicyclo[2.2.2]oct-1-yl cations bearing at C(2) or C(3) an imine (**14–17**), methylidene (**18**, **19**), dicyanomethylidene (**20**, **21**), carbonitrile (**22**, **23**), or nitro functions (**24**, **25**). Our quantum mechanical calculations predict that the (*E*)-imino group, and likewise the oxo group, can behave as an electron-releasing homoconjugated substituent because of favorable through-bond n(C═NH) ↔ σ(C,C) ↔ p(C$^+$) interactions.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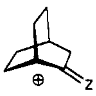
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16 Z=(E)-NH
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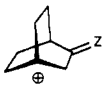
20 Z=$C(CN)_2$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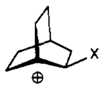
19 Z=CH_2
21 Z=$C(CN)_2$


22 X=CN
24 X=NO_2


23 X=CN
25 X=NO_2

Table I. AM1 Calculated Heats of Formation (ΔH_f, kcal/mol) of Cations 11–25 (R^+) and Neutrals (RH) 26–33. AM1 Relative Hydride Affinities (ΔDH, kcal/mol) of Cations 11–25[a]

ion/molecules	ΔH_f	$\Delta H_f(R^+)$ – ΔH_f(RH)	ΔDH[b]	$\Delta\Delta H_f$[c]
11 (X = H)	183.0	219.1	(0.0)	
12 (2-oxo)	173.2	234.7	15.6	5.9
13 (3-oxo)	167.3	228.8	9.7	
14 (2-(*Z*)-NH═)	218.5	228.8	9.7	5.0
15 (3-(*E*)-NH═)	213.6	223.8	4.7	
16 (2-(*E*)-NH═)	215.6	225.8	6.6	–0.1
17 (3-(*Z*)-NH═)	215.4	225.7	6.7	
18 (2-CH_2═)	208.4	220.7	1.6	0.1
19 (3-CH_2═)	208.3	220.6	1.5	
20 (2-$C(CN)_2$═)	287.0	236.9	17.8	1.8
21 (3-$C(CN)_2$═)	285.2	235.1	16.0	
22 (2-CN)	226.1	228.9	9.8	1.6
23 (3-CN)	224.5	227.3	8.2	
24 (2-NO_2)	204.2	237.4	18.3	2.4
25 (3-NO_2)	201.8	235.0	15.9	
26 (X = H)	–36.1			
27 (ketone)	–61.5			
28 ((*Z*)-NH)	–10.3			
29 ((*E*)-NH)	–10.2			
30 (CH_2═)	–12.3			
31 ($C(CN)_2$═)	50.1			
32 (2-CN)	–2.8			
33 (2-NO_2)	–33.2			

[a] With complete geometry optimization. [b] $\Delta H_f(R^+) - \Delta H_f(RH) - \Delta H_f(\mathbf{11}) + \Delta H_f(\mathbf{26}) = \Delta DH$. [c] ΔH_f(2-substituted) – ΔH_f(3-substituted bicyclo[2.2.2]oct-1-yl cation) = $\Delta\Delta H_f$.

Calculation Methods

Exploratory calculations on cations **11–25** and the corresponding bicyclo[2.2.2]octane derivatives **26–33** were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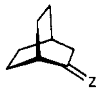
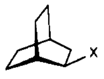

27 Z=O
28 Z=(Z)-NH
29 Z=(E)-NH
30 Z=CH_2
31 Z=$C(CN)_2$


32 X=CN
33 X=NO_2

performed using the semiempirical AM1 parametrization[12] of the AMPAC[13] program (SUN4 work-station). For the smallest systems **11–19** and **26–30**, equilibrium geometries were obtained with the ab initio GAUSSIAN 82,[14] GAUSSIAN 86,[15] or GAMESS[16] programs on CRAY 2, CRAY-XMP, or VAX 8550 computers. The geometries were completely optimized with respect to all bond lengths and bond angles using Berny's method[17] with standard convergence criteria. The size of ions **11–19** and the corresponding hydrocarbons **26–30** limited the basis set at the STO 3G level.

Results and Discussion

The calculated heat of formation of cations **11–25** ($\Delta H_f(R^+)$) and of the corresponding bicyclo[2.2.2]octane derivatives **26–33** (ΔH_f(RH) obtained by the AM1 technique are given in Table I. The differences $\Delta H_f(R^+)$ –

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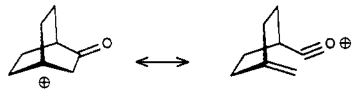
Table II. Ab Initio (STO 3G) Total Energies (E_{tot}, Hartrees) of Ions (R^+) 11–19 and Neutrals (RH) 26–30: Relative Hydride Affinities of Cations 11–19 (ΔE, kcal/mol)

method: ion/molecules	STO 3G^a E_{tot}	$E_{tot}(R^+)^b$ – E_{tot}(RH)	ΔE^c	$\Delta\Delta E^d$
11 (X = H)	–306.65516	521.7	(0.0)	
12 (2-oxo)	–379.28284	537.0	15.3	8.5
13 (3-oxo)	–379.29648	528.5	6.8	
14 (2-(*Z*)-NH=)	–359.74733	537.1	15.4	
15 (3-(*E*)-NH=	–359.76161	528.5	6.8	8.6
16 (2-(*E*)-NH=)	–359.75530	532.5	10.8	
17 (3-(*Z*)-NH=)	–359.76133	528.3	6.6	4.2
18 (2-CH_2=)	–344.00949	526.0	4.3	
19 (3-CH_2=)	–344.01389	523.3	1.6	2.7
26 (X = H)	–307.48658			
27 (ketone)	–380.13865			
28 ((*Z*)-NH)	–360.60322			
29 ((*E*)-NH)	–360.60382			
30 (CH_2=)	–344.84777			

^{a} With complete geometry optimization. ^{b} In kcal/mol. ^{c} $\Delta E = E_{tot}(R^+) - E_{tol}(RH) - \Delta E_{tot}(\mathbf{11}) + E_{tol}(\mathbf{26})$, in kcal/mol. ^{d} Difference in stability between 2- and 3-substituted bicyclo[2.2.2]oct-1-yl cation isomers, in kcal/mol.

ΔH_f(RH) correspond to the hydride affinities of cations R^+ minus $\Delta H_f(H^-)$. The relative hydride affinities of the 2- and 3-substituted bicyclo[2.2.2]oct-1-yl cations with respect to the unsubstituted ion **11** are given by the differences $\Delta DH = \Delta H_f(R^+) - \Delta H_f(RH) - \Delta H_f(\mathbf{11}) + \Delta H_f(\mathbf{26})$. As expected[18] for electron-withdrawing substituents such as Z = oxo, imine, methylidene, $C(CN)_2$ or X = CN, NO_2, the hydride affinity for the substituted bicyclo[2.2.2]oct-1-yl cations were calculated to be higher than that of the unsubstituted ion **11**. Because of the difference in electronegativities between the O, N, and C atoms, the destabilization of the 2-substituted bicyclo[2.2.2]oct-1-yl cations decreases in the order **12** > **14**, **16** > **18** (compare ΔDH values, Table I). The destabilization effect of the 2-(dicyanomethylidene) (see **20**) and 2-nitro (see **24**) substituents are about the same whereas that calculated for the 2-cyano group (see **22**) is smaller and comparable with those found for the 2-(*Z*)-imino group (see **14**).

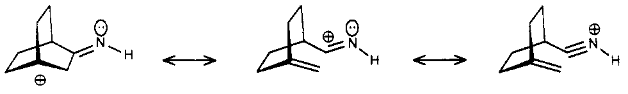
As expected for (–I) substituents, the destabilization effect was calculated to be larger for the 2-substituted than for the 3-substituted bicyclo[2.2.2]oct-1-yl cations because the distance separating the substituents and the carbenium ion center $C(1)^+$ is smaller in the former than in the latter ions. This differential substituent effect is very small for the 2-methylidene- and 3-methylidenebicyclo[2.2.2]octyl cations (**18** vs **19**) and somewhat larger for the dicyanomethylidene- (**20** vs **21**) and nitro-substituted derivatives (**24** vs **25**). It is interesting to note, however, that for latter cations the differential substituent effect did not surpass 2.5 kcal/mol (AM1 calculations) whereas it amounted to 5.9 and 5.0 kcal/mol for the oxo and syn-imino substituents, respectively (compare $\Delta\Delta H_f$ values, Table I). Striking was the finding that the anti-imino isomers **16** and **17** did not show the same differential substituent effect! Interestingly, the predictions based on the semiempirical AM1 calculations (Table I) were confirmed by the ab initio STO 3G MO calculations (Table II). They confirmed the predictions made above (compare the $\Delta\Delta E$ values), i.e. the 3-oxobicyclo[2.2.2]oct-1-yl (**13**) and 3-(*E*)-iminobicyclo[2.2.2]oct-1-yl cations (**15**) are more stable than expected for ions perturbed by electron-withdrawing (–I) substituents. This can be interpreted in terms of the intervention of a stabilizing effects due to the polarizability of systems **13** and **15**. These electron-donating effects are proposed to be associated with through-bond $n(CO) \leftrightarrow \sigma C(2),C(3) \leftrightarrow pC(1)^+$ and $n((E)\text{-}C{=}NH) \leftrightarrow \sigma C(2),C(3) \leftrightarrow p(C(1))^+$ interactions in 3-oxobicyclo[2.2.2]oct-1-yl cation (**13**) and 3-(*E*)-iminobicyclo[2.2.2]oct-1-yl cation (**15**), respectively, interactions which can be represented by the limiting structures **13** ↔ **13′** and **15** ↔ **15′** ↔ **15″**, respectively.



13 13'

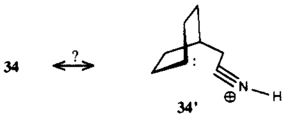
Such interactions are less favorable in the 3-(*Z*)-iminobicyclo[2.2.2]oct-1-yl cation (**17**) because the n(C=NH) electron pair in this system does not overlap with the σC(2),C(3) bond as well as in the case of the *E* isomer **15**.

The model **15** ↔ **15′** ↔ **15″** suggests that this cation adopts some triple bonded C≡N character in its equilibrium geometry. The more the limiting structure **15″** contributes, the easier it should be to interconvert the 3-(*E*)-imino (**15**) into the 3-(*Z*)-iminobicyclo[2.2.2]oct-1-yl cation (**17**), and vice-versa.[19] In order to test this hypothesis we have evaluated the energy barriers of the *Z* ⇄ E interconversions for the 2-imino (**14** ⇄ **16**), 3-imino cations (**15** ⇄ **17**) and for the corresponding neutral imines (**28** ⇄ **29**) with the AM1 technique. Our results are summarized in Table III and confirm our model **15** ↔ **15′** ↔ **15″**. Indeed, the energy barrier for process **17** → **15** (transition state **35**) was found to be significantly lower than that calculated for **16** → **14** (transition state **34**) and for **29** → **28** (transition state **36**).[20] The comparison of the geometries obtained for **34**, **35**, and **36** (Table III) show that, as in the ground-state **15** which admits limiting structure **15′**, the transition state **35** admits a significant contribution of limiting structure **35′**. This was indicated by the relatively long C(2)–C(3) bond calculated for **35** compared with that found in transition states **34** and **36**.



15 15' 15''

The lowering of the energy barrier for the interconversion of the 2-iminobicyclo[2.2.2]oct-1-yl cations **14** ⇄ **16** compared with that of the neutrals **28** ⇄ **29** is not readily explained. According to our semiempirical calculations showing a C(1)–C(2) bond lengthening in **34** compared with that calculated in **14**, **16** (see supplementary material) and **35** (Table III), we can propose that the limiting structure **34′** contributes to **34**. However, this proposal must be taken caustiously as long as it is not confirmed by higher level MO calculations.



34'

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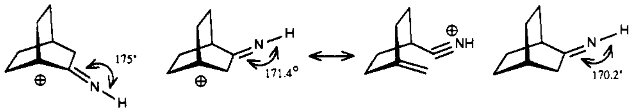
Table III. AM1 Transition States 34, 35, and 36 for the Interconversions 14 ⇄ 16, 15 ⇄ 17, and 28 ⇄ 29, Respectively. Heat of Formations, ΔH_f (kcal/mol); Bond Lengths, Å



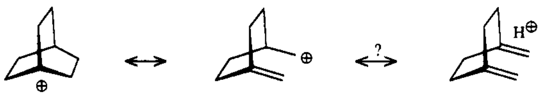
	34	**35**	**35'**	**36**
ΔH_f	: 231.2	225.6		11.6
Barrier (Z→E)	: 15.6	$\boxed{12.0}$		21.9
C=N	: 1.218	1.214		1.241
N-H	: 0.968	0.969		0.958
C(2)-C(3)	: 1.554	$\boxed{1.617}$		1.518

Table IV. Comparison of the σC(2),C(3), σC(5),C(6), and C=Z Bond Lengthenings in 3-Substituted Bicyclo[2.2.2]oct-1-yl Cations Compared with the Corresponding Hydrocarbons (in Å)

	$\Delta l_{2,3} - \Delta l_{5,6}$[a]		$\Delta l_{C=Z}$	
cation	AM1	STO-3G	AM1	STO-3G
13, Z = O	0.019	0.030	-0.019	-0.013
15, Z = (*E*)-NH	0.013	0.021	-0.019	-0.011
17, Z = (*Z*)-NH	-0.001[b]	0.007	-0.013	-0.009
19, Z = CH_2	-0.011	-0.002	-0.003	-0.003
21, Z = $C(CN)_2$	-0.017		-0.010	
23, X = CN	-0.004			
25, X = NO_2	-0.016			

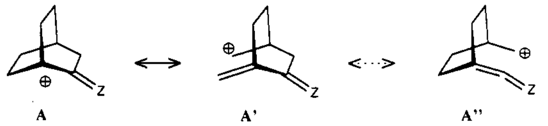
[a] See the supplementary material. [b] Negative values correspond to bond shortenings.

The hypotheses **13** ↔ **13′** and **15** ↔ **15′** ↔ **15″** invoked above for the "extra" stability of the 3-oxo- (**13**) and 3-(*E*)-iminobicyclo[2.2.2]oct-1-yl cation (**15**) were confirmed by the comparison of the calculated geometries of cations **11–25** and of the corresponding bicyclo[2.2.2]octane derivatives **26–33**. On ionizing bicyclo[2.2.2]octane (**26**) into bicyclo[2.2.2]oct-1-yl cation (**11**), the σC(1),C(2), σC(1),C(6) and σC(1),C(7) bonds are shortened while the σC(2),C(3), σC(5),C(6), and σC(7),C(8) bonds are lengthened,[21] in agreement with model **11** ↔ **11′** that implies charge delocalization through favorable σ(C,C) hyperconjugation (good alignment between the $pC(1)^+$ empty orbital and the adjacent σ(C,C) bonds).[23] The C(4)–H bond does not change between **26** (1.089 Å (ab initio STO 3G); 1.125 Å (AM1)) and **11** (1.089 Å (ab inito STO 3G); 1.121 Å (AM1)) contrary to the proposal of Grob and co-workers[22] that implies the doubly hyperconjugated structure **11″** to explain the long-range substituent effects on the S_N1 solvolysis rate constant of 4-substituted bicyclo[2.2.2]oct-1-yl esters.[23]



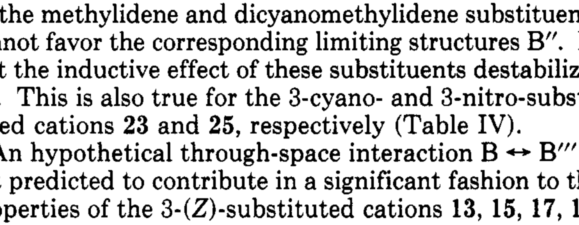
11 11' 11''

On substituting **11** at C(2) with electron-withdrawing groups (e.g. Z = O, NH, CH_2, $C(CN)_2$; or X = CN, NO_2), the charge delocalization in the bicyclic skeleton can be represented by limiting structures A ↔ A′ ↔ A″, the limiting structures A″ contributing less than A′. This is indicated by the comparison of σC(1),C(2) bond shortening ($\Delta l_{1,2}$) and the σC(2),C(3), and σC(5),C(6) bond lenghtening ($\Delta l_{2,3}$, $\Delta l_{5,6}$, see supplementary material) calculated for **12, 14, 16, 18, 20, 22,** and **24**. These findings can be interpreted in terms of dipole/charge repulsions between the charged centers and the substituents which favor structures A′ over A″.



A A' A''

In the case of the 3-substituted bicyclo[2.2.2]oct-1-yl cation the calculated geometries can be interpreted by the limiting structures B ↔ B′ ↔ B″. For the 3-oxo and 3-(*E*)-imino derivatives (**13** and **15**), the corresponding limiting structures B″ are predicted to contribute more than B′ as it was found that the σC(2),C(3) bond lengthenings are larger than those of σC(5),C(6) (Table IV). Interestingly, this differential effect is significantly reduced in the case of the 3-(*Z*)-iminobicyclo[2.2.2]oct-1-yl cation and reversed for the 3-methylidene (**19**), 3-(dicyanomethylidene (**21**), 3-cyano- (**23**), and 3-nitrobicyclo[2,2,2]oct-1-yl cations (**25**)! Thus, as proposed above on the basis of the relative stabilities of 2- and 3-substituted bicyclo[2.2.2]oct-1-yl cations, the n(CO) and n(C=NH) electron pairs in **13** and **15**, respectively, intervene in the stabilization of the corresponding limiting structures B″, i.e. **13′** and **15′**, respectively. These through-bond electron-releasing effects of the homoconjugated carbonyl and (*E*)-imino groups are related to the Grob fragmentation and the frangomeric effect.[24] The unfavorable alignment between the n(C=NH) and σC(2),C(3) bond in the 3-(*Z*)-iminobicyclo[2.2.2]oct-1-yl cation (**17**) prohibits a similar effect. In the case of the **19** and **21**, the absence of n electron pair on the methylidene and dicyanomethylidene substituents cannot favor the corresponding limiting structures B″. In fact the inductive effect of these substituents destabilizes B″. This is also true for the 3-cyano- and 3-nitro-substituted cations **23** and **25**, respectively (Table IV).



An hypothetical through-space interaction B ↔ B‴ is not predicted to contribute in a significant fashion to the properties of the 3-(*Z*)-substituted cations **13, 15, 17, 19,** and **21** as the corresponding C=Z double bond were calculated to be shortened, rather than lengthened with respect to the corresponding hydrocarbons (Table IV). It is interesting to note, though, that the C=Z bond shortening is larger for the 3-oxo- and 3-(*E*)-iminobicyclo[2.2.2]oct-1-yl cations than for the other derivatives.

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Conclusion

AM1 and ab inito STO 3G MO calculations on bicyclo[2.2.2]oct-1-yl cation and 2- and 3-substituted derivatives suggest that the carbonyl and imine functions in 3-oxo- (**13**) and 3-(*E*)-iminobicyclo[2.2.2]oct-1-yl (**15**) cations are less electron withdrawing than expected on the basis of their inductive (through-space) effect because of the intervention of an electron-releasing effect due to favorable through bond n(CO) ↔ σ(C,C) ↔ p(C^+) and n-(C=NH) ↔ σ(C,C) ↔ p(C^+) interactions, respectively.[25] This phenomenon is predicted to be less important in 3-(*Z*)-iminobicyclo[2.2.2]cation (**17**).

Acknowledgment. We are grateful to the Swiss National Science Foundation, the Fonds Herbette (Lausanne), and Hoffmann-La Roche and Co., AG (Basel) for financial support. We thank the Ecole Polytechnique Fédérale of Lausanne (EPFL, CRAY 2 computer), the Swiss Institute of Technology in Zürich (ETHZ, CRAY XMP computer), and Prof. G. Bodenhausen, University of Lausanne (SUN 4), for generous gifts of computing time.

Registry No. **11**, 22907-76-2; **12**, 129314-99-4; **13**, 129315-04-4; 14, 129315-00-0; **15**, 129315-05-5; **16**, 129315-01-1; **17**, 129315-06-6; 18, 129315-02-2; **19**, 129315-07-7; **20**, 129315-03-3; **21**, 129315-08-8; **22**, 129315-09-9; **23**, 129447-11-6; **24**, 129315-10-2; **25**, 129447-12-7; **26**, 280-33-1; **27**, 2716-23-6; **28**, 129315-11-3; **29**, 129315-12-4; **30**, 2972-20-5; **31**, 129315-13-5; **32**, 6962-74-9; **33**, 5437-58-1; H^-, 12184-88-2.

Supplementary Material Available: Atomic coordinates, bond lengths, and bond angles calculated (completely optimized geometries) by the AM1 method for **11–36** and by the STO 3G techniques for **11–19**, **26–30** (81 pages). Ordering information is given on any current masthead page.

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Amino Alcohol and Amino Sugar Synthesis by Benzoylcarbamate Cyclization

Spencer Knapp,* Paivi J. Kukkola, Shashi Sharma, T. G. Murali Dhar, and
Andrew B. J. Naughton

Department of Chemistry, Rutgers-The State University of New Jersey, New Brunswick, New Jersey 08903

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The sodium anion (**3**) of an alcohol-derived benzoylcarbamate (**2**) may be used to deliver an amino nitrogen intramolecularly to electrophilic carbon centers such as bromides, epoxides, and triflates, giving rise to amino alcohol and amino diol derivatives of general form **4–6**. A procedure for selective monotriflation of carbohydrate diols is described that exploits the enhanced reactivity of carbohydrate hydroxyls flanked by a cis, vicinal ether oxygen. Subsequent benzoylcarbamate formation and cyclization allows the conversion of several sugars to amino sugars (**47**, **54**, **74**, **80**). However, the cyclization occurs on the carbonyl oxygen if the triflate site is hindered (**63** and **67**).

For the synthesis of amino compounds, intramolecular delivery of a nitrogen nucleophile sometimes offers advantages over the intermolecular variant. An extensive family of cyclization methods has been developed that allows the synthesis of amino compounds with excellent control over the position and the stereochemistry of the amino group, while minimizing the extent of competing elimination or rearrangement side reactions.[1,2] We recently introduced,[3] coincidentally with McCombie's group,[4] the benzoylcarbamate cyclization method for the synthesis of amino alcohol and amino diol derivatives from precursors bearing a hydroxy group and a nearby electrophilic carbon center. In this paper we present the full description and experimental details for these transformations and also describe their further application to the preparation of amino sugars.

The concept of an alcohol-derived benzoylcarbamate **2** as a likely intramolecular source of nucleophilic nitrogen arose because [1] such derivatives should readily form under neutral conditions (**1** → **2**),[5] [2] the anion **3** of a benzoylcarbamate should be easily generated and stable toward reversion to the original alcohol,[6,7] but still possess sufficient negative charge at nitrogen to undergo *N*-

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