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# ELECTRONIC STRUCTURE AND CONFORMATIONAL EQUILIBRIA OF PHENYL-PROPYLCARBOCATIONS[a]

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**Abstract**—Modified CNDO calculations were performed on different conformations of various phenyl propyl cations and related compounds. Molecular energies and electronic structures are presented and discussed. A substituted secondary benzyl cation, the 1-phenyl-1-propyl carbocation (**12**) is found to be the most stable isomer. The open chain 1-phenyl-2-propyl carbocation (**11b**) has a lower energy than the propylene benzenium cation (**11d**). In contrary, previous calculations of 2-phenyl-1-ethyl cation lead to the result that in this case the ethylene benzenium cation is the most stable structure. Rotational barriers for different substituted 1-propyl and 2-propyl cations were calculated. The results are explained by hyperconjugative stabilization.

## INTRODUCTION

Carbocations were postulated as reactive intermediates as early as the second part of the last century and became an important factor of reaction mechanisms in organic chemistry. With the exception of some unusually less reactive examples, e.g. triphenyl carbenium ion, no spectral and structural data of carbocations were available until quite recently Olah[1] succeeded in the preparation of almost all important types of classical and nonclassical cations in extremely acid solns. Almost at the same time semiempirical and *ab initio* LCAO-MO-SCF-calculations on carbocations were published.[2–9,15,16,19,20,23] Very accurate calculations are now available for the smallest carbocations $CH_5^+$ and $C_2H_5^+$.[9] They give a reliable picture of the most stable structures in the vapor phase. In the case of $C_2H_5^+$ the nonclassical bridged carbocation has the lowest energy. Unfortunately all attempts to prepare small primary carbenium ions in solution have not been successful. Hence no direct comparison of the most stable structures in the vapor phase and in solution can be made with our present knowledge.

The organic chemist, however, is mainly interested in larger carbocations, which cannot be calculated by *ab initio* methods with large basis sets because of the enormous numerical requirements. Hence approximations have to be made. In order to find out, which approximate method is sufficiently reliable and most economic for a particular case, the results of various semiempirical methods and *ab initio* calculations with basis sets of different size on ethyl and vinyl carbocations are compared in Table 1. Two general conclusions can be drawn: the common semiempirical methods (CNDO, INDO, MINDO, NDDO) overemphasize the stability of nonclassical, bridged carbonium ions. *Ab initio* calculations with small basis sets on the contrary give too low energies for the classical carbonium ions. An extension of the basis set reduces the energy difference between the two structures. Near the Hartree–Fock limit both structures **1a** and **1b** have almost the same energies. The bridged carbocation is slightly preferred. Very recent calculations by Zurawski *et al.*[9] including electron correlation using a version of the independent electron pair approximation (IEPA-PNO[13,14]) on the Et cation show an additional stabilization of the nonclassical structure **1b** by correlation energy. The surprisingly good agreement between the IEPA- and modified CNDO (MODCNDO[17–19]) calculations must be accidental. However, compared with the much more expensive *ab initio* calculations using medium size basis sets the CNDO formalism modified by Kollmar *et al.* (MODCNDO) seems to be a reliable approach for calculations on larger carbocations at least concerning relative energies. Among all the other semiempirical proce-

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[a] Dedicated to Prof. Dr. F. Hecht at the occasion of his 70th birthday.

[b] The author to whom reprint requests should be sent.

Table 1. Relative stabilities of classical and bridged ethyl and vinyl carbocations calculated by different LCAO-MO-SCF methods

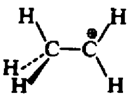
| Method of calculation | | E(**1b**)–E(**1a**) (kcal/mole) | E(**2b**)–E(**2a**) (kcal/mole) | Ref |
|---|---|---|---|---|
| semiempirical | NDDO | $-33.2$ | $-32.0$ | 2 |
| | MODCNDO | $-10$ | $-6$ | 3 |
| *ab initio* without electron correlation | 7, 2/2 (?)[a] | 1 | | 4 |
| | STO-3G | 11·4 | | 6 |
| | 6, 3/3(2, 1/1) | | | |
| | 4-31G | 7·3 | 19·2 | 7 |
| | 8, 4/4(3, 2/2) | | | |
| | 6-31G | 6·7 | 19·2 | 7 |
| | 10, 4/4(3, 2/2) | | | |
| | 10, 5/4(4, 2/2) | | 18·5 | 5 |
| | 10, 5/5(3, 5/2) | 8·8 | | 8 |
| | 10, 4, 1/4(3, 2, 1/2) | 0·4 | 7·4 | 7 |
| | 10, 4, 1/4, 1(3, 2, 1/2, 1) | $-0.9$ | 5·7 | 7 |
| | 10, 6, 1/6, 1(6, 4, 1/4, 1) | $-1$ | 5 | 9 |
| *ab initio* with electron correlation | IEPA[b] | $-9$ | $-7$ | 9 |

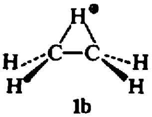
[a] The basis sets applied are denoted in the following way: a, b, c/d, e(a′, b′, c′/d′, e′) means as-, bp- and cd-gaussian functions at the C atom contracted to a′s-, b′p- and c′d-groups and similarly ds- and ep-gaussian functions at the hydrogen atom contracted to d′s- and e′p-groups. The specific notations applied by Pople and coworkers, STO-3G, 4-31G and 6-31G are described in detail in the original papers.[10–12]

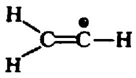
[b] IEPA = Independent electron pair approximation based on Pseudonatural orbitals (PNO'S).[13,14]

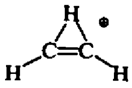
dures this method gives by far the best results for carbocations.

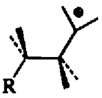
Carbocations containing phenyl groups are of special interest in preparative and theoretical organic chemistry. Stabilization by conjugation and particular neighbouring group effects have been discussed extensively.[37,38] Because of their size, however, only a few reliable MO calculations on phenyl substituted carbocations are available. Phenylethyl cations have been studied in detail by Hehre.[23] The most stable conformation of this cation is not the primary carbenium ion (**7a**) but a symmetric, bridged ethylenebenzenium cation (**7b**). The same result was obtained by an analysis of the $^{13}C$ and $^{1}H$ NMR spectra of phenylethyl cations in solution.[24,25] The homologous series of phenylpropyl cations (**6**) has not been investigated. Hence it seemed interesting to obtain some information on the stable conformations of these cations and to study the influence of the phenyl group at different positions of the propyl side chain. In this paper, MODCNDO studies on stable conformations and rotational barriers of phenylpropyl cations and related compounds are reported.


**1a**

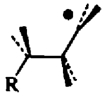

**1b**


**2a**

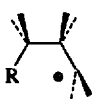

**2b**



**a**



**b**

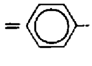


**c**

3: R = H

4: R = $CH_3$

5: R = $(CH_3)_2CH$

6: R = 

## *Method of calculation*

The CNDO formalism developed by Pople *et al.*[21] was applied in all our calculations. The computer program QCPE 141[22] written by Dobosh was modified according to the suggestions of Kollmar and Fischer.[17,18]

The molecular geometries were calculated from standard bond lengths and bond angles summarized

Table 2. Bond lengths and bond angles used in the MODCNDO calculations

| Structure(s) | Bond(s) | Type | R (Å) | Angle(s) |
|---|---|---|---|---|
| **3, 4, 5, 6, 12** | C—C | aliphatic | 1·54 | ∢CCC = 109·472° |
| | C—H | aliphatic | 1·09 | ∢HCH = 109·472° |
| **6, 8, 11a–11c, 12** | C—C | aromatic | 1·397 | ∢CCC = ∢CCH = 120° |
| | C—H | aromatic | 1·084 | |
| **6, 11a–11c** | C—C | $C_{aliphat.}$–$C_{aromat.}$ | 1·52 | |
| **3, 4, 5, 6** | C—C | $C^+$—C | 1·49 | ∢$HC^+H$ = ∢$HC^+C$ = 120° |
| | C—H | $C^+$—H | 1·12 | |
| **8** | C—C<br>C—H | cyclopropane | taken from Ref 15 | |
| | C—C | $C_{cyclopropyl}$–$C_{phenyl}$ | 1·46 | |
| **9, 10, 11** | C—C | $C^+$—C | 1·49 | ∢$C_1C_2C_3$ = 130° |
| | C—H | $C^+$—H | 1·12 | ∢$C_1C_2H_{13}$ = ∢$C_3C_2H_{13}$ = 115° |
| **12** | C—C | $C^+$—$C_{phenyl}$ | 1·40 | ∢$C_2C_3C_4$ = 130°<br>∢$C_2C_3H_{15}$ = ∢$C_4C_3H_{15}$ = 115° |

in Table 2. For a number of less common molecular geometries the values were taken from energy minimized *ab initio* calculations. Rotations around the most interesting bond were calculated explicitly point by point with different angular increments.

For two examples the canonical CNDO orbitals were localized by the method described by Boys.[26,27] A computer program, which is part of the CNDO/LOCI program[28,29] was used. The notation used for the individual atoms is shown in Fig. 1.*

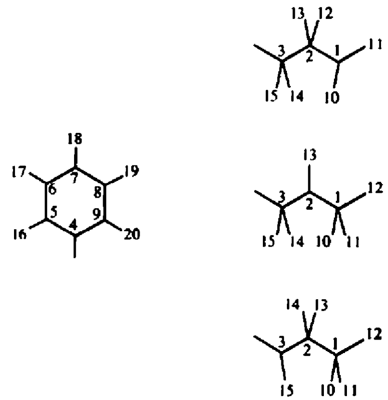


Fig 1. Notation for the atoms in phenyl propyl cations

## RESULTS

The relative energies of different isomeric and rotameric structures of phenylpropyl cations are summarized in Table 3. The net charges of the phenyl groups indicate different degrees of delocalization in the isomeric cations.

In the case of different 1-propyl carbocations rotational barriers were investigated in detail. The energy difference between the eclipsed and perpendicular conformations **a** and **b** was taken as a measure for the energy barrier of the rotation around the $C_1C_2$ bond. The values for a series of differently substituted 1-propyl cations are summarized in Table 4. Similarly the rotational barriers around the $C_2C_3$ bond in 2-propyl carbocations were calculated as the differences in energy between the eclipsed and perpendicular conformations, **a** and **b** (Table 5).

Table 3. Relative energies and net charges of the phenyl groups in different isomeric phenyl propyl cations $C_9H_{11}^+$ (MODCNDO calculations)

| Ion or conformation | | ΔE (kcal/mole)[a] | $q_{C_6H_5}$[b] |
|---|---|---|---|
| Corner protonated phenyl cyclopropane | | | |
| bisected | **8a** | 30·3 | 0·213 |
| perpendicular | **8b** | 20·1 | 0·221 |
| 3-Phenyl-1-propylcation[c] | | | |
| synperiplanar, perpendicular | **6c** | 18·8 | 0·187 |
| antiperiplanar, eclipsed | **6a** | 7·7 | 0·206 |
| antiperiplanar, perpendicular | **6b** | 0 | 0·238 |
| Propylenebenzeniumion | **11d** | −3·6 | |
| 1-Phenyl-2-propylcation[d] | | | |
| eclipsed/eclipsed | **11c** | −14·7 | 0·245 |
| perpendicular/eclipsed | **11a** | −26·2 | 0·249 |
| perpendicular/perpendicular | **11b** | −27·7 | 0·301 |
| 1-Phenyl-1-propylcation | **12** | −32·9 | 0·445 |

[a] The energy of the most stable conformation of 3-phenyl-1-propyl cation was assumed to be the zero of the energy scale.

[b] Net charge of the phenylgroups $q_{C_6H_5} = \sum_{i=4}^{9} q_i + \sum_{i=16}^{20} q_i$ the numbers of the individual atoms are shown in Fig 1.

[c] Syn- and antiperiplanar characterizes the rotational state around the $C_2C_3$ bond, eclipsed and perpendicular denotes the rotation around the bond $C_1C_2$.

[d] Analog to c, the first notation concerns the $C_2C_3$, the second the $C_1C_2$ bond.

Potential curves for the rotation around the bond $C_2$—$C_3$ in 3-phenyl-1-propyl (**6**) and 1-butyl cation (**4**) are shown in Fig 2. The angle *θ* is defined as the dihedral angle between the planes $C_1C_2C_3$ and

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*The calculations were performed on a Univac 494 Computer at the Rechenzentrum Graz and an IBM 360/44 Computer at the Interfakultäres Rechenzentrum, Universität Wien.

Table 4. Rotational barriers and changes in orbital populations in substituted 1-propyl-carbocations[a]

| | | | Rotational barrier (kcal/mole) | | P(4)[c] | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | MODCNDO | | | STO-3G[15,16] | | |
| Structure | R | R[b] | MODCNDO | STO-3G[15,16] | a | b | $P_b-P_a$ | a | b | $P_b-P_a$ |
| 3 | H— | $CH_3$— | 5·2 | 2·5 | 0·121 | 0·156 | 0·035 | 0·133 | 0·135 | 0·022 |
| 4 | $CH_3$— | $CH_3CH_2$— | 7·1 | 3·7 | 0·122 | 0·180 | 0·058 | 0·133 | 0·148 | 0·035 |
| 5 | $(CH_3)_2CH$— | $(CH_3)_2CH—CH_2$— | 7·0 | — | 0·131 | 0·193 | 0·062 | — | — | — |
| 6 | $C_6H_5$— | $C_6H_5—CH_2$— | 7·7 | — | 0·128 | 0·209 | 0·081 | — | — | — |

[a] The energy differences between the antiperiplanar, eclipsed (a) and the antiperiplanar, perpendicular (b) conformer of the substituted 1-propyl carbocation represents the rotational barrier around the bond $C_1—C_2$.

[b] In Fig 3 a different notation for the substituent is used.

[c] $P(4)$ is the orbital population of the "empty" $p$-orbital at C1 (*cf* numbers of orbitals in Table 6).

Table 5. Rotational barriers and changes in orbital populations in substituted 2-propylcarbocations[a]

| | | $E_a-E_b$ (kcal/mole) | | P(8)[b] | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Structure | R | MODCNDO | STO-3G[15] | a | b | $P_b-P_a$ | a | b | $P_b-P_a$ |
| 9 | H— | | 0·05 | | | | | | |
| 10 | $CH_3$— | 2·7 | 2·16 | 0·182 | 0·202 | 0·020 | 0·182 | 0·198 | 0·016 |
| 11 | $C_6H_5$— | 2·5 | | 0·185 | 0·233 | 0·048 | | | |

[a] The energy difference between the eclipsed (a) and the perpendicular (b) conformer of the substituted 2-propylcarbocations represent the rotational barrier around the bond $C_2—C_3$.

[b] P(8) is the orbital population of the "empty" $p$-orbital at C2 (*cf* numbers of orbitals in Table 6).

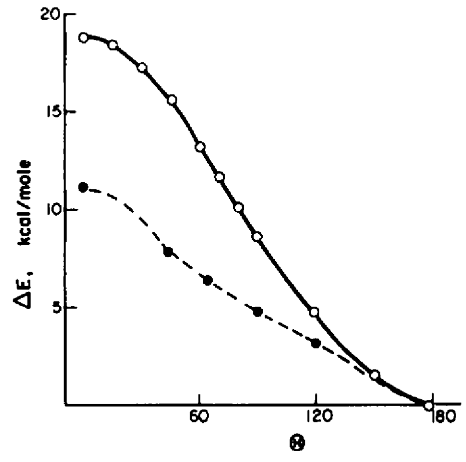


Fig 2. Potential curves for the rotation around the bond $C_2C_3$ in 1-butylcation (**4b**: -●-●-●-) and 3 - phenyl - 1 - propyl cation (**6b**: -○-○-○-○-)

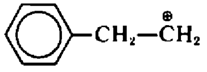
$C_2C_3C_4$. $\theta = 0°$ corresponds to the conformations **4c** and **6c**, $\theta = 180°$ represents the most stable conformers **4b** and **6b**. The canonical CNDO orbitals of **6a** and **6b** were localized. For the phenyl group the expected results consisting of well localized CC and CH $\sigma$-bonds and a more or less delocalized $\pi$ electron system were obtained. All the six CH bonds of the side chain were perfectly localized too ($\Sigma C_{ik}^2 > 0{\cdot}99$). Well localized bonds were obtained with only one exception, the $C_2C_3$ bond in **6b**, where an appreciable contribution of the "empty" $p$ orbital on $C_1$ is found.

## DISCUSSION

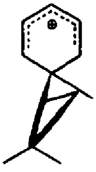
*Total energies*. The relative energies of the isomeric carbocations $[C_9H_{11}]^+$ in Table 3 show the expected decrease in energy in the order primary, secondary and benzylic cations. Contrary to the results on phenyl ethyl carbocations,[23] the bridged propylenebenzenium cation **11d** is less stable than its open chain isomer **11b**. This difference can be explained easily, since in the former case the spirobenzenium cation **7b** has to compete with a primary cation **7a** whereas **11b** is, due to Me substitution, a more stable secondary cation.

The most stable conformation of the primary phenylpropyl cation is **6b**. The relative stability of this antiperiplanar conformer of substituted propyl cations has been explained by hyperconjugative interaction.[16,30] This effect will be discussed in detail together with the rotational barriers in 1-propyl cations. Additionally the structure **6b** is stabilized by a bonding long range interaction between the C atoms 1 and 3 (*cf* localized orbitals), which indicates already the possibility of forming a nonclassical bridged carbonium ion of the type **8**.

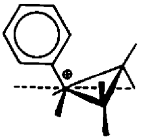
Among the secondary carbenium ions **11** the perpendicular conformation **11b** shows the lowest energy. Again hyperconjugative interaction seems to be responsible for the relative stability of this conformer. The difference in energy between the conformations **11a** and **11c** is unexpectedly large. It



**7a**

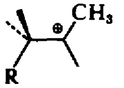


**7b**

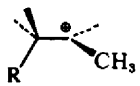


**8a**

**8b**



**a**

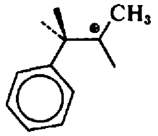


**b**

**9**: R = H

**10**: R = $CH_3$

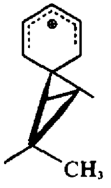
**11**: R = 



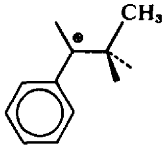
**11c**

can be explained easily by steric hindrance since in **11c** the H atoms 13 and 16 are packed very close together. The distance between them is calculated to 1·37 Å only, whereas the sum of the Van der Waals radii for two hydrogens is 2·4 Å.

In order to find out the influence of the phenyl group on the relative stability of the primary (**6**) and secondary (**11**) propylcations the difference in energy between the most stable conformers was calculated: $\Delta E = E(\mathbf{6b}) - E(\mathbf{11b}) = 27{\cdot}7$ kcal/mole. For comparison this energy difference was calculated for the two butyl cations as well: $\Delta E = E(\mathbf{3b}) - E(\mathbf{9b}) = 26$ kcal/mole. Hence the phenyl group does not change the relative stability of primary and secondary carbocations to any extent as long as it is not attached directly to the cationic center. In the case of the Bu cations *ab initio* and experimental values for this energy difference are available: ΔE(STO-3G) = 20 kcal/mole[16] and ΔE(exp) = 18 kcal/mole. MODCNDO calculations give too large energy differences and overemphasize, therefore, to some extent the relative stability of secondary carbenium ions.



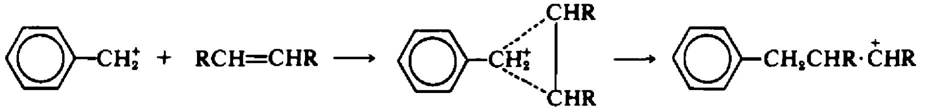
**11d**



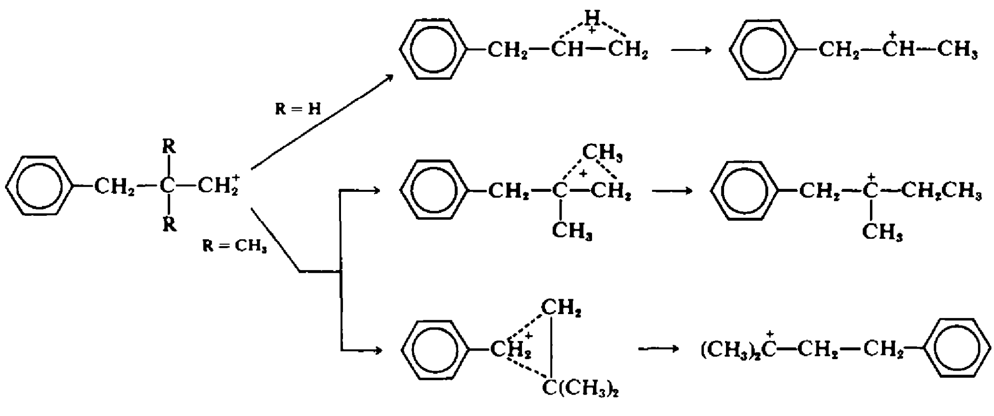
**12**

As expected, the most stable 1-phenyl-propyl carbocation is the cyclopropane benzyl cation **12**.

Species related to corner protonated cyclopropane have been postulated as intermediates in addition reactions of benzyl cations to olefins[39] and in rearrangements of 3-phenyl-1-propyl cations.



(1)



(2)

(3)

(4)

Whereas for the unsubstituted ion only a 1,2 hydride shift was observed (Eq 2),[40] in the 2,2-dimethyl-3-phenyl-1-propyl cation both migration of the benzyl and the Me groups occurred, the latter being favored by a factor of two or three.[41]

Our MODCNDO calculations show that the perpendicular conformation **8b** is about 10 kcal/mole more stable than the eclipsed conformer **8a**. Starting with the energetically less favourable, but stereochemically advantageous conformation **6c**, the rearrangement (2) requires only about 1·3 kcal/mole. Similarly a small energy barrier was found also for the rearrangement of the unsubstituted 1-propylcation.[15] The main difference between the unsubstituted cation and its phenyl derivative, however, is brought about by the conformational preequilibria of the cations. Whereas the MODCNDO energy for the rotation (**3b**→**3a**) prior to the rearrangement amounts only

$$\Delta E = E(\mathbf{3a}) - E(\mathbf{3b}) = 5{\cdot}2\ \text{kcal/mole}$$

in 1-propyl cation, a much higher energy difference is obtained for the corresponding rotation (**6b**→**6c**) in 3-phenyl-1-propylcation,

$$\Delta E = E(\mathbf{6c}) - E(\mathbf{6b}) = 18{\cdot}8\ \text{kcal/mole.}$$

The rotational barriers calculated by the MODCNDO method are certainly too high (*cf* Table 4 or the corresponding part in the discussion), but nevertheless we can conclude from our data that the rate of the rearrangement in 1-propyl cation is reduced appreciably by phenyl substitution in position 3, in agreement with experimental evidence.

### *Population analysis*

First of all the reliability of MODCNDO wave functions and electron densities derived from them had to be proved by comparison with the results of more rigorous methods. Semiempirical and *ab initio* results of calculations on propyl and butyl carbocations are summarized in Table 6. CNDO/2 calculations with the original parametrization lead to net charges at the formally +1 charged C atom, which are far too high. The change in the parameters introduced by Kollmar and Fischer[17,18] improves the results remarkably. The net charges at the cationic center of 1-propylcation as obtained by MODCNDO as STO-3G calculations agree very well. Net orbital and Mulliken overlap populations calculated by the MODCNDO method or with STO-3G basis functions are almost the same for a series of primary and secondary propyl and n-butyl cations. Hence the MODCNDO procedure seems to be equally reliable with respect to wave functions and electron densities for carbocations.

Net charges of the whole benzene rings were calculated in order to estimate the electronic properties of the phenyl groups in phenyl–propyl cations (Table 3). In all structures investigated, the benzene ring carries a positive net charge and hence the phenyl groups acts as electron donor. The maximum charge transfer is found in the benzylic cation **12**. For all classical carbenium ions an interesting parallelism between the net charge of the benzene ring and the energetic stability of the carbocations is found. The corner protonated phenyl cyclopropanes show a relatively high positive charge at the benzene ring and do not fit into the series of the other phenyl propyl cations.

The net charges of the C atoms, which carry the formal positive charge +1, and the orbital populations of the "empty" $p^+$ orbital at the $sp^2$ hybridized cationic center, $P(p^+)$, are summarized for the classical carbenium ions in Table 7. Although an electron density of $0{\cdot}2\ e_0$ only is transferred into the $p^+$ orbital, the net charge of the positive C atom usually does not exceed $+0{\cdot}2\ e_0$ by much. Hence the cationic center is stabilized mainly by $\sigma$ electron donation effects. This result has been described by a number of authors.[19,20] In general a higher electron density at the $p^+$ orbital is associated with a smaller net charge at the cationic C atom. A careful look at Table 7 shows, however, that there are many exceptions on this rule. There is no strict proportionality of charge transfer in the $\sigma$ and $\pi$ electron system. The relative amounts of $\sigma$ and $\pi$ stabilization of the carbenium ions depend on the particular geometry.

In secondary carbenium ions the cationic C atom carries a higher positive charge than in primary carbenium ions. This surprising result was found and discussed extensively by Kollmar and Smith.[20] The benzylic carbocation **12** does not fit into the series of the other secondary phenyl propyl cations. It shows a relatively low positive charge at the cationic center $C_3$ and a high orbital population of the $p^+$ orbital.

### *Localized orbitals*

From population analysis of the canonical orbitals we could expect a bonding interaction between the C atoms 1 and 3 in the perpendicular conformation **6b** of 3-phenyl-1-propyl carbocation. In order to find out the type of long range interaction, the canonical orbitals of **6a** and **6b** were localized. The LO's of **6a** correspond completely to the classical valence bond formula. All electron pairs of the side chain appear in perfectly localized two center orbitals. The degree of localization exceeds 99%. For the conformer **6b** well localized (>99%) two center orbitals are found for all CH bonds and the $C_1C_2$ $\sigma$ bond. In the case of the $\sigma$ bond $C_2C_3$, no two center localization is possible. The $p^+$ orbital at $C_1(2pz)$ contributes with a coefficient of $c_{ik} = -0{\cdot}32$ to this LO. Hence we obtain approximately 10% probability to find the electron at the cationic C atom $C_1$. The whole orbital can be described as a weak three center orbital, which is mainly localized at $C_2$ and $C_3$.

Table 6. Charge densities and population analysis of substituted propylcations calculated by different methods

| | | Net charge $q(C^+)$[a] | | Net orbital population[b] $P(p^+)$ | | Mulliken overlap population[c] $P(p^+p_v^\alpha)$ | | $P(p^+s_H^\alpha)$ |
|---|---|---|---|---|---|---|---|---|
| Structure | CNDO | MODCNDO | STO-3G[15] | MODCNDO | STO-3G[15] | MODCNDO | STO-3G[15] | MODCNDO |
| **1a** | 0·370 | 0·225 | 0·249 | | | | | |
| **3a** | 0·365 | 0·187 | | 0·121 | 0·113 | 0·0571 | 0·0748 | 0·0146 |
| **3b** | | | | 0·156 | 0·135 | 0·0849 | 0·0836 | 0·0044 |
| **4a** | | 0·199 | | 0·122 | 0·133 | 0·0751 | 0·0746 | 0·0147 |
| **4b** | 0·336 | 0·175 | | 0·180 | 0·148 | 0·0898 | 0·0874 | 0·0042 |
| **10a** | | 0·232 | | 0·182 | 0·182 | 0·0649 | | 0·0120 |
| **10b** | 0·352 | 0·224 | | 0·202 | 0·198 | | | |

[a] The net charge $q$ is defined:[35] $q(1) = Z_1 - {}_v\Sigma_1 P_{vv}$; $Z_1$ ... charge of nucleus 1, $P_{vv}$ ... gross atomic population. $C^+$ denotes the carbon atom, which carries the formal positive charge.

[b] The net orbital population is defined:[35] $P(v) = P_{vv} = 2\sum_{k=1}^{m} C_{vk}^2$; $p^+$ denotes the formally empty $p$ orbital of the C atom $C^+$.

[c] In order to be able to compare *ab initio* and MODCNDO results Mulliken overlap population[35] were calculated from our eigenvectors: $P(v) = 2\sum_{k=1}^{n} C_{\mu k}C_{vk} \cdot S_{\mu v} \cdot P_v^\alpha$ denotes the $p$ orbital at the carbon atom ($C^\alpha$) neighbouring $C^+$, which is oriented parallel to $p^+$. $s_H^\alpha$ denotes the $s$ orbital of an H atom at $C^\alpha$.

Table 7. Orbital populations and charge densities of substituted propyl cations (MODCNDO)

| Primary cations | | | Secondary cations | | |
|---|---|---|---|---|---|
| Structure | $q(C^+)^a$ | $P(p^+)^a$ | Structure | $q(C^+)^a$ | $P(p^+)^a$ |
| **3a** | | 0·121 | **10a** | 0·232 | 0·182 |
| **3b** | 0·187 | 0·156 | **10b** | 0·224 | 0·202 |
| **4a** | 0·199 | 0·122 | **11a** | 0·230 | 0·185 |
| **4b** | 0·175 | 0·180 | **11b** | 0·216 | 0·233 |
| **4c** | 0·187 | 0·156 | **11c** | 0·205 | 0·179 |
| **5a** | 0·193 | 0·131 | **12**[b] | 0·176 | 0·348 |
| **5b** | 0·168 | 0·193 | | | |
| **6a** | 0·149 | 0·128 | | | |
| **6b** | 0·161 | 0·209 | | | |
| **6c** | 0·181 | 0·166 | | | |

[a] $q(C^+)$ is the net charge of the carbon atom carrying the formal charge +1, $P(p^+)$ is the orbital population of the "empty" $p$-orbital at this center.

[b] Secondary benzylic carbocation.

### *Rotational barriers*

The calculation of rotational barriers has been a difficult problem and both semiempirical and less extended *ab initio* calculations do not give correct results. A detailed comparison between *ab initio* and INDO energy partitioning for the rotational barrier in ethane was presented by England and Gordon.[31] In general, "steric hindrance" is overemphasized by the CNDO/2 and INDO methods and the calculated barriers are much too high. Usually MINDO or MODCNDO results are more reliable. A comparison of rotational barriers in 1-propyl and 2-propylcarbocations (Tables 4 and 5) calculated by the MODCNDO method, with the results of STO-3G calculations shows that the semiempirical barriers are still somewhat too high. The relative values, however, are reproduced correctly.

### 1-*Propylcarbocations*

Substitution of the H atom in position 3 of 1-propyl carbocation by alkyl or phenyl groups leads to a pronounced increase in the height of the barrier for the rotation around the bond $C_1$—$C_2$. Steric hindrance can be ruled out as the reason for this increase in barrier height because the distance between the substituent R and the rotating unit is very large in the antiperiplanar conformation of the cation. Recently an interpretation of the nature of this rotational barrier by different hyperconjugative stabilization of the two conformers **6a** and **6b** was presented:[30] In the Et cation **1a** "$\pi_x$" and "$\pi_y$" stabilization is the same and only a negligible small sixfold barrier is found. Electropositive substituents however, stabilize the perpendicular conformation **b** (Fig 3) and give rise to a large twofold rotational barrier. Hence in the perpendicular conformation **b** we would expect a higher orbital population of the "empty" $p^+$ orbital—P(4)—than in the eclipsed conformation **a**. Table 4 confirms this suggestion and shows additionally that the rotational barrier increases with increasing difference in P(C1) between the orbital populations of both conformers. As expected the orbital population of the "empty" $p^+$ orbital increases in the perpendicular conformer with increasing electron donating properties of the substituent, whereas it remains almost constant in the eclipsed conformer **a**.

The orbital population calculated by the MODCNDO method agrees well with the STO-3G results.[15,16] In general, the transfer of electron density into the "empty" $p^+$ orbital is somewhat larger in

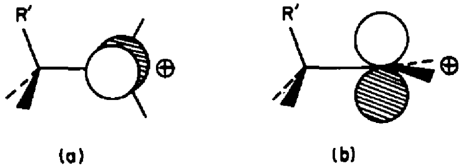


Fig 3. Hyperconjugative stabilization of carbeniumions in the eclipsed (**a**) and perpendicular (**b**) conformation

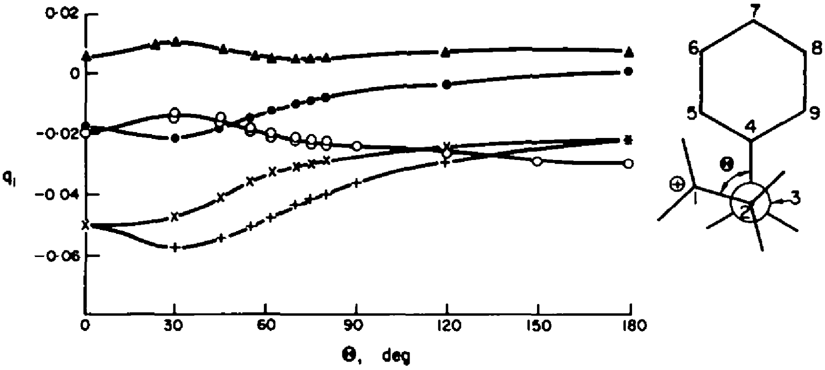


Fig 4. Polarization effects in the benzene ring during rotation around the bond $C_2C_3$ in 3 - phenyl - 1 - propyl cation ($C_4$: - ▲ - ▲ - ▲ - , $C_5$: - + - + - + - + -, $C_6$ - ○ - ○ - ○ - ○ - , $C_7$: - ● - ● - ● - ● -, $C_8$: - ○ - ○ - ○ - and $C_9$: - × - × - × -).

MODCNDO than in STO-3G calculations. This slight exaggeration of the charge transfer by the MODCNDO method explains, at least in part, the too high rotational barriers around the bond $C_1$–$C_2$.

A pronounced influence of the substituent R on the height of the rotational barrier is found also for the rotation around the bond $C_2C_3$ (Fig 2). The potential curve for 1-Bu cation shows an interesting superposition of a small threefold rotational barrier with maxima at the dihedral angles $\theta = 0°$, 120° and 240⁺ (*cf* Fig 5) and a large single barrier with the maximum at $\theta = 0°$. Evidently, the large barrier describes the repulsive interaction between the substituent R and the cationic center $C_1$. The threefold barrier has the same origin as the rotational barrier in ethane and corresponds to the interaction between the H atoms and the CH bonds respectively. In 3-phenyl-1-propyl cation the repulsive interaction between the phenyl group and the cationic center is still larger and hence the slope of the single barrier is so steep that the superimposed threefold barrier can hardly be seen. From the potential curve we can conclude that there is no energetic stabilization of the cation by direct polarization interaction between the positive charge and the phenyl group. Nevertheless small polarization effects can be observed in the charge distribution of the benzene ring, which is represented best by the net charges of the individual C atoms. In the antiperiplanar conformer **6b** ($\theta = 180°$) the net charges of the C atoms show the expected alternant distribution. The highest electron density is observed at the *m* positions 6 and 8. The negative charge is somewhat smaller at the two *o* positions 5 and 9. A still smaller electron density is found at position 7, the *p* C atom with respect to the propyl chain. During rotation around the bond $C_2C_3$ the net charges are changed only slightly as long as the positive C atom $C_1$ does not lie directly above the benzene ring $-180° > \theta > 90°$ (*cf* Fig 5). At smaller values of $\theta$ ($90° > \theta > 0°$) a shift of electron density towards the *o* position of the benzene ring can be observed. The C atom 5, which comes closest to the positive charge of $C_1$, shows the highest electron density, followed by the other *o* C atom 9. In the *m* and *p* positions the electron density is remarkably smaller. At $\theta = 0°$ (**6c**) the two *o* and the two *m* positions of course become equivalent. The net charge of the *o* positions ($q_5 = q_9 = -0{\cdot}05$) is more negative than the almost equal values for the C atoms in *m* and *p* positions ($q_6 = q_8 \sim q_7 \sim -0{\cdot}02$).

### 2-*Propylcarbocations*

In 2-propylcarbocations the rotational barrier around the bond $C_2C_3$ again depends strongly on the nature of the substituent R. The explanation of the origin of the barrier by different hyperconjugative stabilization in the "$\pi_x$" and "$\pi_y$" system[30] can be applied also to this case. At first it seems surprising that the phenyl group gives rise to a smaller barrier than the Me group (Table 5) contrary to the results for the analogous rotation around the bond $C_1C_2$ in 1-propyl cations (Table 4). Regarding the effect of substitution more carefully, however, we find that for the hyperconjugative stabilization in 1-propyl cations we had to compare the electron donor properties of an ethyl and a benzyl group. The benzyl group is the better electron donor and hence leads to the higher rotational barrier. In 2-propyl cations an Me group has to be compared with a phenyl group, where evidently the former is the more efficient electron donor. Therefore the rotational barrier around the $C_2C_3$ bond is higher in the 2-Bu cation than in the 1-phenyl-2-propyl cation.

## CONCLUSIONS

A comparison of our results with experimental and more rigorously calculated *ab initio* data shows, that the modified CNDO method can be applied successfully to the calculation of minimum energy geometries, conformational equilibria and rotational barriers of larger carbocations. In general, only a qualitative or semiqualitative agreement can be expected. Besides the energies the electron distribution is shown to be reliable. Only minor discrepancies in the electron populations obtained by *ab initio* or MODCNDO calculations were found.

The semiempirical treatment is applicable to large cations too and even structures as large as polycyclic carbocations can be investigated with the computers available. One of the most interesting questions in carbocation chemistry concerns the influence of counter ions and solvent molecules on the most stable structures of the cations. With all the data available now no definite answer to this question can be given. The use of semiempirical methods, however, offers a possibility to study the ion together with its solvation shell and we may expect some results in this field in the near future.

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