The Configuration of Organic Carbanions

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The configurations of organic carbanions are studied using the MINDO/1 and MINDO/2 methods. It is found that the stability of the pyramidal configuration increases on going to small ring cyclic carbanions. Conjugation to an olefinic group decreases the inversion barriers of pyramidal carbanions but does not lead to their planarization. Conjugation to a nitro group, however, causes the planarization of the carbanions. It is found that the monosolvation of methyl-carbanion increases its planarization energy.

The growing interest in the chemistry of organic carbanions requires the accurate description of their geometries and electronic configurations. The knowledge of the geometric conformation at the ionic site is important for the discussion of the observed retention and racemization processes in carbanionic reactions. Extensive solvation of the carbanions as well as their association with the gegenions [1] in solution make the experimental study of their structure a difficult task. Although there have been recent gas phase studies of carbanion reactions [2], no conclusions about their configurations could be drawn from these studies. For these reasons we feel that a theoretical analysis of the geometries and electronic configurations of the different carbanions is essential and may provide usefull informations about their structures.

Both theoretical and experimental studies suggested a pyramidal configuration for the unsubstituted open chain carbanions [1–3]. The height of the inversion barrier increased on going from the methyl- to the cyclopropyl carbanion. In the following text we report a molecular orbital study of the stable configurations of some cyclic carbanions with different ring size and the required activation energies for their configuration changes. Further, the influence of the strong electron withdrawing nitro group, in the α-position to the carbanion site, is studied. We applied the MINDO/1 method for the evaluation of the heats of formation of both planar and pyramidal configurations of the carbanions, in a similar manner as had been published before. The inversion energy is defined as;

$$\Delta E^{\ddagger}_{\text{inversion}} = \Delta H_{\text{f, pyramidal}} - \Delta H_{\text{f, planar}} \,. \quad (1)$$

We applied the MINDO/2 method for the calculation of the equilibrium geometries of the ions. However, no quantitative values for the inversion barriers should be expected from the application of this method [4].

The Methyl Carbanion

The published value for the inversion barrier of this carbanion, with a pyramidal ground state is 20.2 kcal/mol (MINDO/1) [5]. To calculate the equilibrium geometry of the ion we used the MINDO/2 rather than the MINDO/1 method due to the known inadequacy of the second method to predict molecular geometries [3]. The calculation included a complete variation of all geometric parameters of the ion, maintaining the C_{3v} symmetry. Figure 1 shows the calculated hypersurface of the ion ($r = C-H$ bond length and ϑ = angle formed by the H atom and the C_{3v} axis).

The energy minimum of the hypersurface corresponds to a value 114° and a C–H bond distance 1.196 Å (including the 0.1 Å elongation that

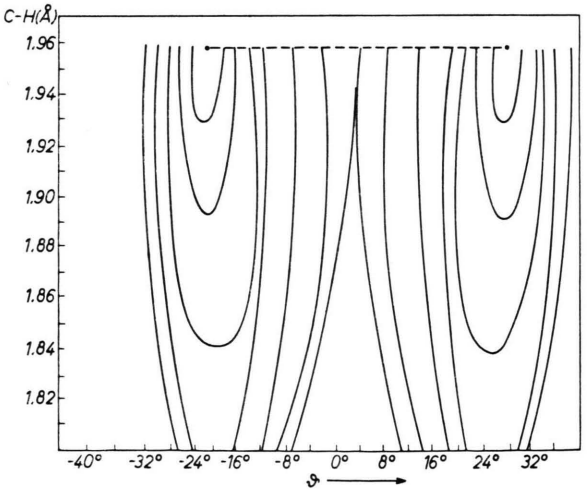


Fig. 1. MINDO/2 calculated energy hypersurface of the CH_3 carbanion (r_{C-H} in Å and ϑ in degrees).

is specific for the MINDO/2 calculation). The hypersurface shows that the inversion process goes through a planar (D_{3h}) transition state and does not cause a change in the C – H distance. The calculated C – H bond is longer than the $C_{sp}3$ – H and $C_{\bar{sp}}2$ – H bonds in neutral molecules. The calculated heat of formation of the ion is 41.5 kcal/mol.

Cyclic Carbanions

Recent molecular orbital (MO) calculations showed that the configurations of cyclic carbanions [5] and radicals [4] depend on the size of their rings. The calculated inversion barrier of the cyclopropyl carbanion was bigger than that of the methyl anion. Experimental results also suggest higher inversion barriers for the nonconjugated cyclopropyl anions [6]. We have carried out MINDO/1 calculations for the three, four and five membered ring carbanions as well as the bridge head anions of some bicyclic systems. MINDO/1 standard bond lengths and angles have been applied through out the calculation. Table 1 shows the calculated inversion barriers for the different cyclic carbanions.

$\Delta E^{\#}_{inv.}$ (kcal/mol)	
	34.4
	15.34
	25.10
	17.51
	27.22
	26.24
	28.29
	anti 7.50 syn 6.70
	17.44

Table 1.
MINDO/1 calculated inversion barriers of some cyclic carbanions (kcal/mol).

The values of Table 1 show a decrease in the inversion barriers with increasing ring size. The only exception forms the cyclopentyl carbanion which has a higher inversion barrier than cyclobutyl carbanion. Introduction of a double bond in the α-position to the ionic site causes a decrease in the inversion barrier in all cases. The decrease in the barrier follows the order, cyclopropyl > cyclobutyl > cyclopentyl. The nondirectly conjugated double bond in the cyclopentenyl carbanion causes a slight increase in the barrier height. Apparently two main factors influence the barrier heights of these carbanions; a) the conjugation to a double bond, b) the variation in the bond angle at the ionic site.

The calculated inversion barrier for the bridge head bicycloheptyl carbanion is lower than that of the cyclopentyl carbanion. This result may be due to the increase in the bond angle (113° in bicycloheptyl- and 108° in cyclopentane). The analysis of the energy change accompanying an inversion process [7] indicates that it is mainly due to the change in the nondiagonal one electron core hamiltonian expectation values;

$$H^{C}_{ij} = \beta_{ij} S_{ij} (I_i + I_j) \; . \qquad (2)$$

In the applied MINDO/1 model the valence bond distances are kept constant during the inversion process. Thus, for the directly bonded C_1, C_2 and C_3 atoms (Fig. 2) the H_{ij} values remain constant

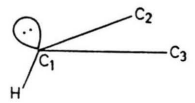


Fig. 2.

(S_{ij} is constant due to the constant distances). Similarly the C_1 – H bond maintains its overlap value during the same process. However, the C_2 – H and C_3 – H distances change as a result of the inversion. The change in these distances depends obviously on the size of the $C_1 - C_2 - C_3$ bond angle. Figure 3

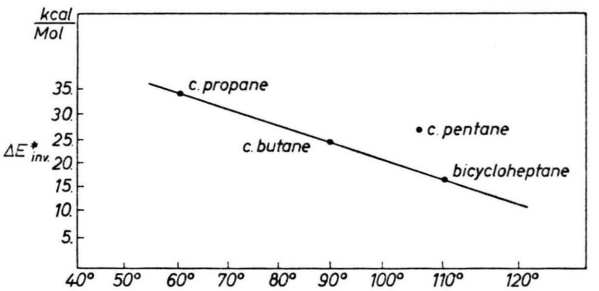


Fig. 3. Correlation of the calculated inversion barriers (kcal/mol) to the $C_1C_2C_3$ bondangles of cyclic carbanions.

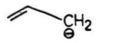
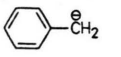
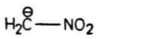
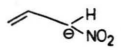
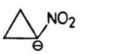
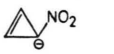
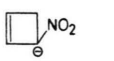
shows the correlation of the calculated inversion barrier to the C – C – C bondangle of some cyclic carbanions.

The Conjugated Carbanions

In a preliminary report we showed that the conjugation of an inverting carbanionic center to a

double bond decreases its inversion barrier [4]. We have extended this treatment to some other conjugated carbanions, particularly those with α-nitro group. Table 2 shows the calculated inversion barriers for some conjugated carbanions.

Table 2. MINDO/1 calculated inversion barriers of conjugated carbanions (kcal/mol).

	$\Delta E^{\#}_{inv.}$ (kcal/mol)
	17.38
	15.63
	− 1.64
	−13.65
	− 1.70
	− 4.70
	− 6.95

Compared with the unsubstituted methyl carbanion, both allyl and benzyl carbanions are calculated to have smaller inversion barriers. Accordingly, the conjugation to an olefine system decreases the barrier height but does not lead to the planarization of the carbanion. The conjugation to the strong electron withdrawing $-NO_2$ group stabilizes the planar configuration. Such carbanions, with unsymmetric substituents, should undergo complete racemization. Similar racemization is expected for the α-sulfonium carbanions.

The Solvated Carbanion

The influence of solvents on the configuration stability of carbanions was recognized experimentally [1]. Asymmetric solvation was postulated as the cause of configuration retention of some carbanions that were expected to invert rapidly [1]. To study the solvation influence we have carried out MINDO/2 calculations for the monohydrated methyl carbanion ($H-O-H\ldots CH_3$). The following geometric parameters have been varied, a) the $C\ldots H$ bond-length (6.5 − 1.5 A); b) $H\ldots C-H$ bondangle (125° − 90°). The $C-H$ bonddistance was kept constant (1.196 Å) and the eclipsed conformation maintained through out the calculation. At the beginning of the calculation the relative stabilities of the exo-(I) and endo-(II) forms were calculated with constant $H\ldots C-H$ bondangle (115°) but different $H\ldots C$ distance (1.5 − 4.0 Å). Conformation (II) was found more stable through out the range of bond distances. It was chosen for the rest of the calculation.

Table 3 shows the calculated ΔH_f values (kcal/mol) of (I) and (II) with different $H\ldots C$ distances.

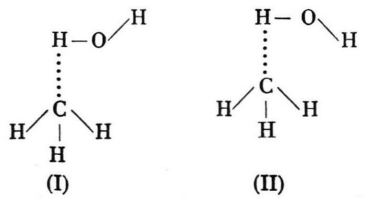


Table 3. MINDO/2 calculated heats of formation of the eclipsed monohydrated methyl carbanion with different $H\ldots\ldots CH_3$ distances (kcal/mol).

$H\ldots\ldots C$	ΔH_f(I)	ΔH_f(II)
4.0	−15.71	−21.0
3.5	−15.13	−21.5
3.0	−14.34	−21.5
2.5	−13.52	−22.0
2.0	−11.74	−21.0

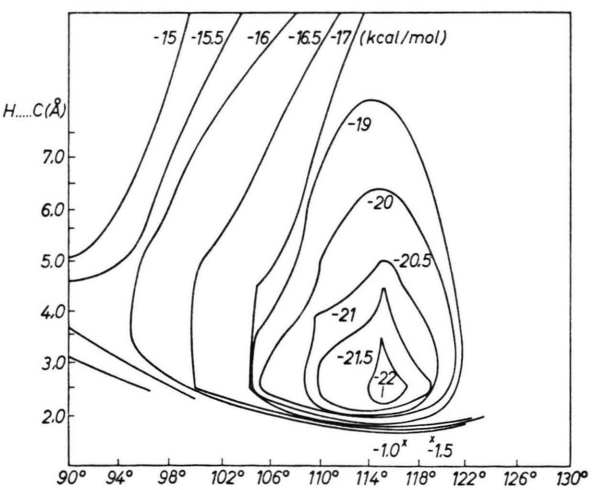


Fig. 4. Calculated segment of the potential hypersurface for the monohydrated methyl carbanion.

Figure 4 shows the calculated segment of the potential hypersurface for the monohydrated methyl carbanion. Other segments of the hypersurface (longer $H-O$ and shorter $H\ldots C$ distances) are not

considered, since they should correspond to the products of the chemical reaction ($CH_4 + OH^-$).

The energy minimum on the plotted hypersurface corresponds to the values 115° and 2.5 Å. The bondangles are therefore equivalent to the bondangles of the nonsolvated methyl carbanion. The transition towards the planar conformation (90°) causes an increase in the energy of the ion. The required energy for the planarization of the ion (6.5 kcal/mol) is bigger than the planarization energy of the nonsolvated methyl carbanion (5.3 kcal/mol).

Acknowledgement

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