Commentationes

Semi-Empirical All-Valence-Electron SCF Calculations of Acidities of Cycloalkanes

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CNDO/2 calculations of the energy change $RH \rightarrow R^- + H^+$ for cycloalkanes give the acidity order: cyclohexane > cyclopentane > cyclobutane > cyclopropane, exactly the reverse of the experimental order. INDO results are similar to CNDO/2. A new method, IRDO, related to NDDO is described. Both of these methods give results differing from the first two but agreement with experiment is still poor.

CNDO/2-Berechnungen der Energieänderung der Reaktion $RH \rightarrow R^- + H^+$ für Cycloalkane gibt folgende Reihenfolge für die Acidität: Cyclohexan > Cyclopentan > Cyclobutan > Cyclopropan, was genau der umgekehrten experimentellen Reihenfolge entspricht. INDO Resultate sind den CNDO/2 Resultaten ähnlich. Eine neue Methode, IRDO, die der NDDO verwandt ist, wird vorgeschlagen. Diese Methoden führen zu Resultaten, die sich von denen der beiden ersten unterscheiden, aber die Übereinstimmung mit dem Experiment ist noch immer unbefriedigend.

Des calculs CNDO/2 de la variation d'énergie de la réaction $RH \rightarrow R^- + H^+$ pour les cyclo-alkanes donnent l'ordre des acidités à l'inverse de l'ordre expérimental: cyclohexane > cyclo-pentane > cyclobutane > cyclopropane. Les résultats INDO sont semblables à ceux de CNDO/2. Une nouvelle méthode, IRDO, liée à NDDO est décrite. Ces deux méthodes donnent des résultats différents des deux premières, mais l'accord avec l'expérience reste faible.

With the growing use of semi-empirical SCF methods related to the CNDO/2 method it is necessary to emphasize the limitations of this method. The optimum parameters are known to depend on the particular properties investigated [1, 2]. Furthermore, in a recent study of arylmethyl cation and aromatic carbanions as reaction intermediates, we found that charge delocalization and charge-dipole interactions were not scaled on the same basis by the CNDO/2 method [3] and that carbanion lone pairs are inadequately handled [4]. Nevertheless, within groups of related compounds, good correlations have been found frequently with experimental reactivities. We would consequently expect that the CNDO/2 method should be reasonably well adapted to the correlation of the kinetic acidities of small-ring hydrocarbons.

Rates of tritiodeprotonation of such cycloalkanes with cesium cyclo-hexylamide in cyclohexylamine have been determined recently and appear to be reasonable measures of the relative energy differences between hydrocarbon and cycloalkyl anion [5]. The logarithms of the relative rates are proportional to the s-character of the C-H bond as measured by $J_{C^{13}-H}$ and may, in the

Table 1. Δ Energies (eV)[a]

	$\log k_{rel}$ Relative Acidity[b]	CNDO/2	INDO	IRDO	NDDO
Benzene	3.1	−0.628	−0.796	−0.350	−0.347
Cyclopropane	0.0	0.0	0.0	0.0	0.0
Cyclobutane	−3.4	−0.287	−0.274	+0.085	+0.081
Cyclopentane	−4.1	−0.457	−0.449	−0.155	−0.004
Cyclohexane (axial)	−4.8	−0.633	−0.490	−0.271	−0.222
Cyclohexane (equatorial)		−0.397	−0.326	+0.072	+0.158

[a] Energy for removal of a proton from a hydrocarbon with respect to cyclopropane.

[b] Relative rates of tritiodeprotonation of cycloalkanes with cesium cyclohexylamide (Ref. [5]).

usual way, be expected to be also proportional to a potential energy difference as given by a molecular orbital calculation.

CNDO/2 calculations were performed using the Pople, Santry and Segal [6] parameters and "standard" geometries. The structures of the hydrocarbons had C-C bonds of 1.54 Å and C-H bonds of 1.09 Å. The anions were derived by removing one proton from the hydrocarbons. Geometries were not varied in this study as we were merely looking for the pattern of results. The CNDOTWO program was obtained from QCPE [7]. The energies calculated for removing a proton from each of several cycloalkanes are summarized in Table 1. These energy changes give an order of decreasing acidity of: cyclohexane > cyclopentane > cyclobutane > cyclopropane, exactly the reverse of the experimental order!

One major deficiency of the CNDO method is the assumption of spherical orbitals for the purpose of calculating the electron repulsion integrals. We expect that this deficiency would be especially severe for the calculation of anions. The effective localization of a large amount of negative charge at the center of the anionic carbon rather than in a sp^3-like lone pair away from the atom should over-emphasize electron repulsion effects. This effect was noted in our previous calculations of aromatic carbanions [4]. This effect shows up in the present work in the profound delocalization of negative charge over the entire molecule, even distant hydrogens, as shown by the charge distributions summarized in Table 2. Thus the calculated acidity order appears to be an artifact; the larger the carbanion, the more atoms can spread the negative charge to escape the excessive electron repulsion.

At the time the CNDO/2 method was introduced by Pople, Santry and Segal, an NDDO (neglect of diatomic differential overlap) method was proposed also [6, 8, 9]. However, to date, no extensive calculations have been performed by this method, partly because of the large number of integrals which are required for moderate to large sized molecules. Some modifications of the NDDO method have appeared and do seem to show some promise [10, 11]. The INDO method includes all of the one-center terms that are included in the NDDO while the other terms are essentially those of CNDO [10]. In order to reduce the number of integrals necessary for the NDDO approximation, one possibility is to set equal to zero those which are small, as in the PNDO method of Dewar and Klopman [11].

Table 2. Charge distributions

Cyclopropane

Method	Hydrocarbon		Anion					
	H	C	H_1	H_2	H_3	C_1	C_2	$C_1 + H_1$
CNDO/2	+0.008	−0.016	−0.109	−0.104	−0.100	−0.447	−0.018	−0.556
INDO	+0.027	−0.054	−0.034	−0.083	−0.085	−0.591	−0.020	−0.625
IRDO	+0.060	−0.120	−0.057	−0.003	+0.012	−0.616	−0.173	−0.673
NDDO	+0.037	−0.074	−0.061	−0.027	−0.041	−0.605	−0.099	−0.666

Cyclobutane

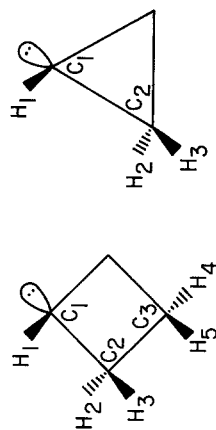| Method	Hydrocarbon		Anion								
	H	C	H_1	H_2	H_3	H_4	H_5	C_1	C_2	C_3	$C_1 + H_1$
CNDO/2	−0.005	+0.010	−0.101	−0.109	−0.102	−0.079	−0.072	−0.435	+0.050	+0.008	−0.536
INDO	+0.012	−0.024	−0.034	−0.095	−0.092	−0.058	−0.046	−0.576	+0.063	−0.039	−0.610
IRDO	+0.019	−0.038	−0.087	−0.071	−0.040	−0.056	−0.042	−0.575	−0.031	+0.046	−0.662
NDDO	+0.016	−0.032	−0.072	−0.063	−0.062	−0.021	−0.017	−0.587	−0.012	−0.026	−0.659

Fig. 1

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Alternatively, we may make the observation that the effects due to the directionality of p-orbitals will get greatly smaller as the centers which contain the orbitals get further apart. The dominant terms will be between atoms which are "nearby", e.g. bonded. This suggests a method in which the CNDO/2 type terms are used for atoms which are not bonded but NDDO terms are used for atoms which are bonded. We will refer to this as the IRDO (Intermediate Retention of Differential Overlap) method.

Two advantages accrue immediately from this type of treatment. The number of integrals which need to be calculated is now directly proportional to the number of atoms in the molecule, rather than to the square. If "standard" geometries are used, an integral calculating routine need be used only once for each type of bond. For example, if all C-H bonds in a molecule are taken to be 1.09 Å long, the C-H integrals need to be calculated only once. Coordinate transformations can then be used to obtain the values for a particular C-H bond. A disadvantage which may be imagined is that the result is dependent on the arbitrary choice of which atoms are bonded and which are not. In practice this would not appear to be a serious restriction, although one would expect to be wary in such structures as "non-classical" carbonium ions. In the limit of very small molecules or systems where all atoms are "bonded" the method reduces to the NDDO method. In the limit of no "bonded" atoms the method reduces to the INDO or CNDO methods.

The integrals necessary were calculated by the program DIATOM [7b] which was incorporated into an extensively modified CNDOTWO program. All electron repulsion integrals of the type (ij/kl) (where i and j are on the same atom and k and l are on the same atom) were used as obtained from this program. In order to make the nuclear attraction integrals $(\mu|V_B|v)$ as obtained from DIATOM compatible with the CNDO/2 assumptions the relation, $V_{AB} = Z_B \gamma_{AB} [(\mu|V_B|v)/(s|V_B|s)]$, was used. We see that for an s-orbital this is the familiar CNDO/2 relation. It was found that if this relation was not used, then predicted bond lengths were much too short as in CNDO/1, where this relation is also not used. All other integrals, including one-center integrals, were not modified. The values of the core terms, $V_{\mu\mu}$, used were those based on Pople's values for the INDO case (C_{2s} −11.02; C_{2p} −2.577; H −7.176) [10].

We thus see that by "bonding" all atoms we have the NDDO method in a way which derives directly from CNDO/2. The CNDO/2, INDO, IRDO, and NDDO methods thus form a graded series and the results from them should be readily comparable.

Calculations by the four methods yielded energies which were within 3% of each other for any one species. Table 1 presents the relative energies for proton removal with respect to cyclopropane. Benzene is added for comparison. Although the CNDO/2 method correctly predicts that benzene is more acidic than the cycloalkanes, this result does not inspire confidence in view of the CNDO/2 predictions of the cycloalkanes. Note also that the inclusion of the one-center terms (INDO method) results in little difference from the CNDO/2 method. The inclusion of the one-center terms alone still does not result in proper handling of anion lone-pairs. Since this appears to be a fundamental limitation resulting from lack of directionality in two-center electron repulsions it seems

unlikely that this limitation can be avoided by simple reparametrization. Consequently, the recent MINDO calculations of gas phase acidity of alcohols [12] and the observed correspondence to the experimental acidity order may be purely fortuitous.

The NDDO results, however, are substantially different. Cyclopropane *is* predicted to be more acidic than cyclobutane, but, unfortunately, the trend is not continued. Cyclopentane is predicted to be about as acidic as cyclopropane and the differences in calculated acidity for the axial and equatorial hydrogens of cyclohexane appear to be much too high. The IRDO results parallel the NDDO results.

Table 2 indicates some of the differences in charges as predicted by the four methods. We present the results for cyclopropane and cyclobutane and their anions. The atoms referred to are shown in Fig. 1. There does not seem to be any great discrepancy between the charges as shown by any one method; all of the methods appear generally to distribute negative charge to all atoms, particularly the hydrogen atoms. It seems significant, however, that the total charge on the carbanionic carbon and its attached hydrogen is higher in the cases where NDDO terms are introduced. This is as expected if the repulsion terms are overemphasized in the CNDO/2 method.

We may conclude that repulsion integrals for anionic species must be calculated on the basis of directional orbitals. It is therefore probably true that any species with lone pairs will also be incorrectly calculated by CNDO type methods. In addition, we should note that making changes of this type does not change some of the other problems inherent in CNDO calculations [2–4]. For example, atomization energies are still high because our basis parametrization has not changed. However, it is clear that the optimum parametrization should be based on a theory which can handle lone pair electrons. It appears that the IRDO modification may be able to handle many molecules adequately. Although it is clear that some differences from the NDDO method must exist in the IRDO modification, correlations of behaviour in many cases would probably be extremely similar. Although the correlations between the experimental acidities and the IRDO and NDDO calculations are still unsatisfactory *with the parameters used*, the *pattern* of the overall results encourages the search for optimum parameters.

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