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OPTIMAL GEOMETRICAL PARAMETERS FOR THE CNDO/2 APPROXIMATION

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Abstract—A set of geometrical parameters is proposed which yields a point in the energy well of organic molecules very close to the minimum in the CNDO/2 approximation.

The CNDO/2 MO method[1] has been widely utilized in studies of chemical structure and reactivity.[2,3] It still remains one of the most frequently applied MO methods in spite of the recent increased use of *ab initio* MO methods, due mainly to more efficient computational methods and to faster, less expensive and more widely available computers, and of the continuing appearance of improved versions of the MINDO procedure.[4]

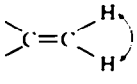
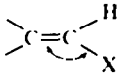
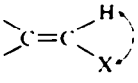
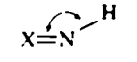
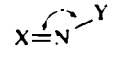
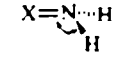
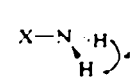
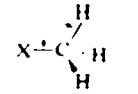
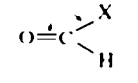
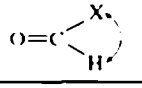
Essentially three types of geometrical parameters have been used as input for the CNDO method: (i) experimental geometries; (ii) "standard parameters"[2] which correspond to averaged experimental values; and (iii) optimized geometries, that define a minimum in the potential energy surface calculated for the molecule. This last treatment has not been widely applied since the procedure of optimization is often lengthy and expensive and furthermore, in many cases results agree closer with experiment when either experimental or standard geometries are used.[5] Nevertheless there exist some instances where the full minimization procedure is the only reasonable approach. This is typically the case of reactive intermediates or of comparisons between these and ground states.

Table 1. Bond lengths and angles

I. Bond lengths

Bond[a]	Length	Bond[a]	Length	Bond[a]	Length
C4–H	1.119	C3–C3	1.442	N2—O2	1.273
C3–H(gem)	1.112	C3–C2	1.419	C3=C3	1.321
C3–H(isol)	1.119	C3–N3	1.398	C3=C2	1.304
C2–H	1.092	C3–N2	1.285	C3=N2	1.285
N3–H	1.071	C3–O2	1.358	C3=O1	1.267
N2–H	1.072	C3–F1	1.339	C2=C2	1.297
O2–H	1.034	C2–C2	1.401	C2=N2	1.266
C4–C4	1.457	C2–N3	1.375	C2=O1	1.239
C4–C3	1.449	C2–N2	1.377	N3=O1[b]	1.224
C4–C2	1.425	C2–O2	1.339	N2=N2	1.221
C4–N3	1.408	C2–F1	1.319	N2=O1	1.194
C4–N2	1.404	N3–N3	1.337	C2≅C2	1.205
C4–O2	1.367	N2–N2	1.326	C2≅N1	1.191
C4–F1	1.343	N3–O2	1.281	C3=C3	1.385[c]

II. Bond angles

Type of angle	Value	Type of angle	Value	Type of angle	Value
	113.2		127.6		114.1
	109.4		112.9		109.1
	112.8		110.8		126.3
			117.4		

[a]The number besides the atom refers to the number of substituents attached to it. Bond lengths are given in Å and angles in degrees.
[b]Partial double bonds in nitro group.
[c]Aromatic bonds.
[d]Torsion angle.

It is the purpose of this work to provide a list of values for geometrical parameters which closely approach the optimal geometry in the CNDO/2 approximation.

RESULTS AND DISCUSSION

Geometry optimization was carried out on simple molecules by variation of each parameter successively. Recently however more efficient geometry optimization procedures have been coupled with the CNDO method.[4] Optimal values obtained for some parameters are summarized in Table 1.†

It is frequently the case with reactive intermediates that varying amounts of electron delocalization obscure the analysis of geometrical parameters in terms of a unifying table. In such cases, the appropriate parameters (or those from which to start an optimization procedure) may be determined by considering the relative contribution of the most important resonance structures and applying to each of them the values in the Table. For example, an initial guess for the CC bond length in the allyl anion would be 1/2 (C3=C3 + C3–C3) = 1.381 A. The optimum value actually found is 1.373 A.[7]

This approach has been applied with success to a variety of problems of organic chemistry such as polyfunctional catalysis,[7] protonation of diazomethane[8] and of diazocarbonyl compounds,[9] acidity of substituted methanes,[10] conformational analysis of 6-membered rings.[9] Thus, geometry optimization not only widens the scope of the CNDO/2 method rendering it applicable to problems where standard geometries lead to unreliable results, but also avoids the arbitrariness of other choices of geometrical parameters.

†A list of the molecules calculated and their optimized geometries is available upon request. It should be noted that substantial discrepancies between optimal and experimental values are found in some cases. Discussions of this problem have been offered.[7]

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