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ON THE USE OF CNDO/2 CALCULATIONS OF MOLECULAR CHARGE AND/OR SPIN DISTRIBUTIONS FOR CHEMICAL PREDICTIONS

J. BURDON and I. W. PARSONS*
Department of Chemistry, University of Birmingham, P.O. Box 363, Birmingham B15 2TT

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Abstract—Caution is recommended in the uncritical use of charge or spin densities, calculated by the CNDO/2 method, for chemical predictions. In particular, it is shown that serious errors may arise either through a poor choice of geometry or through ineffective convergence of the relevant density matrices.

Ever since the release of CNDO/2 computor programs for general use,[1,2] many authors (e.g. Refs. 3–15) have used this technique to calculate charge and/or spin densities in molecules and ions of interest to them. On occasion[3,6,10,12–15] such calculations have been used as the bases for mechanistic predictions. In this communication, we wish to sound a warning note concerning acceptance of such data (and predictions). There seem to be two principle areas of difficulty.

First, care must be taken to establish, if at all possible, a reasonable approximation to the true (equilibrium) geometry. The most obvious ways to do this are via an X-ray study of a related molecule or via energy minimisation in CNDO/2, but these are clearly both counsels of perfection. This is important because, as we now show, it is possible to force a particular charge or spin distribution by (in)judicious choice of geometry.

Secondly, some cases may require care to ensure proper convergence.

We illustrate these difficulties with examples drawn from our recent work on highly fluorinated species, and with calculations on the allyl cation and radical which are designed to make the points more simply.

The first point, the close interdependence of geometry and electron distribution, is in one sense trivial, since the molecular orbital approximation is, at least in the Hartree-Fock-Roothaan Formalism,[16] conceptually equivalent to setting up isolated atoms at the particular geometry to be used and then permitting the electrons in the various orbitals to migrate over the whole molecule so as to establish the best energy, and hence best set of orbitals. Put like this, it is clear that the degree of interaction between atomic orbitals on different nuclei will depend upon geometry. The point we emphasise is that this dependence—at least for π-systems—is *strong*: that misleading charge and/or spin densities may be calculated (correctly) if the geometry is unrepresentative of the molecule. These misleading results may then be used to make mechanistic predictions which will clearly be suspect.

Other authors (e.g. Ref. 4) have clearly been aware of this point, even though they may, for other reasons, and despite changes in relative charge densities on changing the geometry, have subsequently chosen a less likely geometry. Nevertheless, it is difficult to avoid the conclusion that some authors have chosen their geometries for ease of trigonometrical calculation rather than for chemical realism.

We illustrate the problem with two sets of calculations. First (Table 1), the allyl cation and radical; the calculations marked *b* are those now referred to. Clearly, in both cases, altering the geometry strongly affects the electronic populations, and the best geometry for the cation—that with the lowest energy—is not the same as that for the radical. Thus, we have a case where any prediction of reactivity based upon a single geometry would be very suspect.† The most important point here is that the choice of a geometry which resembles a single resonance canonical (e.g. $CH_2{=}CH{-}CH_2^+$ with C=C as 1·32 Å and C–C as 1·5 Å) inevitably produces a correspondingly distorted electronic distribution.

We further illustrate this difficulty over geometry with some calculations on perfluoro-2-pyridinonium-cations and -radicals (Table 2). We performed three calculations for each species; one with a skeletal geometry representing essentially a 1,3-diene structure (**A**), one representing a 1,4-diene (**C**), and one a delocalised species (**B**). The angles in each geometry were arrived at by a hand-iterative procedure, attempting to minimise the overall distortions in the angles (from 120° or 109°28′) for fixed bond lengths. Clearly, this is to some extent a matter of judgement, although *minor* variations in geometry, for **B** at least, made very little difference to spin densities or charges. The delocalised species **B** had a superior energy for both the cation and the radical, and the energy advantages were quite substantial; it corresponds quite closely to the experimentally determined[17] geometry for pyridine hydrochloride.

The point we again emphasise is that the geometries **A** and **C**, which resemble particular resonance cononical forms, force the *electron densities* into resembling these canonical forms. Indeed, predictions of positional reactivities in, for example, ionic reactions, based on the geometries shown here, would differ; geometry **C** would lead to prediction of predominant *para* (to CF_2) attack by nucleophiles, whereas geometry **A** would suggest *ortho*. Thus it is possible to get into a sequence of argument wherein a poor choice of geometry gives an unrealistic electron distribution, which is then used to predict—falsely—reaction at a particular position: this is very difficult to detect if no geometry variation is performed.

Of the calculations shown here, geometry **B** may be

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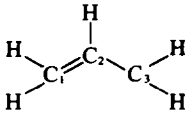
†Of course, even if the predicted inequality of bond lengths in the radical were correct (and there seem to be no relevant studies in the literature) rapid interconversion of the two forms would nullify differential reactivity at room temperature: nevertheless, the main point stands.

Table 1. CNDO/2 calculations[a] on the allyl systems

Numbering as in 

$\widehat{C_1C_2C_3} = 120°$

$\widehat{HCC} = 120°$

C_1–C_2 (Å)	C_2–C_3 (Å)	No. of iterations	Energy (a.u.)	C_1	C_2	C_3
				+ charges in cation		
1·32	1·51	6[b]	−24·3640	0·275	0·030	0·386
1·34	1·48	6[b]	−24·3761	0·288	0·032	0·370
1·36	1·45	6[b]	−24·3841	0·302	0·033	0·355
1·38	1·42	6[b]	−24·3876	0·317	0·033	0·341
1·40	1·40	6[b]	−24·3890	0·329	0·033	0·329
				spin densities in radical		
1·32	1·51	9[b]	−24·6476	0·037	0·212	0·750
1·34	1·48	11[b]	−24·6474	0·058	0·202	0·740
1·36	1·45	16[b]	−24·6437	0·116	0·153	0·731
1·36	1·45	75[c]	−24·6444	0·228	0·047	0·725
1·38	1·42	30[b]	−24·6390	0·330	−0·021	0·691
1·40	1·40	22[b]	−24·6384	0·508	−0·107	0·599
1·40	1·40	31[d]	−24·6387	0·539	−0·114	0·575
1·40	1·40	43[c]	−24·6388	0·553	−0·115	0·562
1·40	1·40	62[e]	−24·6388	0·557	−0·115	0·558

[a] QCPE program 91 as modified for our ICL 1906A by Dr. D. W. Davies; parameters are as given in Ref. 22; convergence to the energy criteria given below.

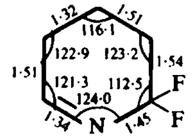
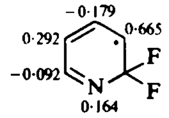
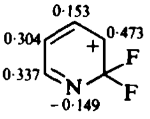
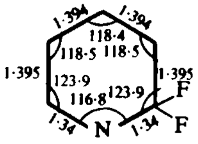
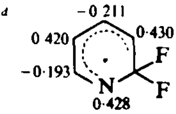
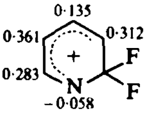
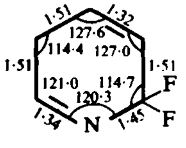
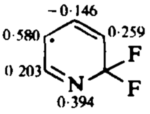
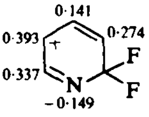
[b] Converged to 0·0001 a.u.

[c] Converged to 0·000001 a.u.

[d] Not yet converged to criterion *c*, but better than *b*.

[e] Converged to 0·00000001 a.u.

Table 2. CNDO/2 calculations[a] on polyfluoropyridine based systems

Geometry	Spin densities (relative energies)	+ ve Charge densities (relative energies)
	(A)[b]  (E[c] = 23 kcal/mole)	 (E[c] = 30 kcal/mole
	(B)[b,d]  (E[c] = 0 kcal/mole)	 (E[c] = 0 kcal/mole)
	(C)[b]  (E[c] = 19 kcal/mole)	

All unmarked bonds are C–F bonds.

[a] As *a* of Table 1; all calculations converged to an energy criterion of 0·0001 a.u.

[b] All =C–F bonds were 1·33 Å and equiangular with the geminal C–C bonds. The CF_2-group C–F bonds were 1·34 Å with C–C–F = 109°28′; the bisector of C–C–F was equiangular with the geminal C–C and C–N bonds.

[c] Relative energies, with the energy for geometry B set to zero.

[d] A Calculation with N–CF_2 = 1·47 Å and CF_2–C = 1·52 Å gave virtually the same densities for both radical and cation.

expected to lead to the most realistic population analyses, since it gives the lowest energies.

The second major point arose out of our investigation of the first one: it is that the usual criteria for convergence of the calculations may not always be satisfactory. In most CNDO/2 calculations, that is, those employing the usual programmes, the criterion for convergence of the SCF cycle is based upon the electronic energy. This energy criterion is generally accepted as satisfactory (or, at least, the publications imply this, albeit some do not state what convergence criterion is being employed), although some authors (e.g. Refs. 3, 10) have used density matrix criteria; we now show that there are occasions when the energy criterion is clearly unsatisfactory.

This difficulty arises because a density matrix converges towards its self-consistent value more slowly than does the energy. Consequently, situations may arise in which the energy has converged to a pre-set criterion but the electronic populations are a long way from their true expection values. Thus, the charge, or spin, densities may be in serious error even though the calculation has apparently converted properly and the geometry is a good one.

We illustrate this point with our results for the allyl radical (Table 1). In our hands the difficulty arises less commonly with cations than with radicals, and we have no substantial experience of anions. This observation is perhaps not unexpected, since the trouble is presumably based in the unrestricted Hartree-Fock formalism used in these radical calculations:[18] the formation of two entirely separate sets of molecular orbitals, interacting only via the density matrix, must slow down the convergence to some extent, and the spin density is the (small) difference between the (large) α and β spin densities at a particular centre.

Consider the calculations shown (Table 1) for the various geometries of the allyl radical. The calculations which have the greater numbers of iterations (those marked *c*, *d*, *e*) have been allowed to converge to smaller than usual energy criteria. In every case, the further iterations have *substantially* altered the calculated spin distributions, and this effect is extraordinarily marked in the case of the symmetric geometry, where a very large number (62) of iterations is required to permit the calculated spins to become (nearly) equal. In this case, of course, the final converged spins must be equal, and any variation from this clearly represents an error in the implementation of the calculation. The point we wish to make is that there may be other cases—unless due care is exercised—where spin densities may not be converged, but where this will remain undetected because of the lack of obvious symmetry in the molecule. An example of this is shown for the 1·36/1·45 Å geometry, where pursuit of convergence beyond our usual limit results in a very substantial rearrangement of spin density. Howland and Flurry[19] have noted a similar phenomenon—slower convergence of density matrix than energy—in some neutral molecules, but the effects were smaller than those described here.

In summary, therefore, we warn against uncritical acceptance of chemical predictions based on CNDO/2 calculations. (We have no reason to suppose that other methods[20,21] are superior from this point of view). If the geometry is unrepresentative—as has commonly been the case with large molecules—or if electronic distributions are not properly converged to their self-consistent values, then serious errors of prediction may occur despite apparently successful calculations.

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