CNDO Molecular Orbital Calculations. On the Invariance of Methods for Second Row Elements

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Abstract: A CNDO method for molecules with second row atoms, in which certain one-center off-diagonal Fock matrix elements are modified, is shown not to be invariant with respect to rotation of the molecular coordinate system. The consequences of this lack of invariance for problems pertaining to molecular conformations are examined, and an invariant version of the method is given.

CNDO molecular orbital theory, which is at present widely used for a variety of molecular problems, has been found to be remarkably satisfactory for the calculations of equilibrium molecular geometries.[2,3] The theory, as originally formulated by Pople and coworkers, maintains rotational invariance which is essential for problems of molecular geometry, at least with respect to rotation of the total coordinate system for the molecule,[4] and invariance to hybridization. Two methods, designated here as A[5] and B,[6] have been developed for the extention of CNDO/2 calculations to second row elements (Na to Cl). Both with and without the inclusion of 3d orbitals in the basis set, they satisfactorily accommodate the equilibrium bond angles for a variety of small molecules. Method B also provides reasonable agreement between calculated and observed dipole moments. The methods differ in their parametrizations, which are derived in part from spectral data (A) and from comparisons with reference SCF calculations (B), and, more significantly, in the treatment of certain off-diagonal matrix elements involving second row atoms. Although the parametrizations for methods A and B are provisional and are not intended for routine calculations on molecules with second row atoms, both methods have been widely used in a number of recent studies.[7]

Method A maintains invariance with molecular rotation. The purpose of this paper is to point out that *results obtained with method B are not rotationally invariant* and to demonstrate some consequences of this.

Results and Discussion

In CNDO theory the off-diagonal Fock matrix elements are given by[2]

$$F_{\mu\nu} = H_{\mu\nu} - {}^1\!/_2 K P_{\mu\nu}\gamma_{AB} \qquad (1)$$

where $H_{\mu\nu}$ is the core Hamiltonian element, $P_{\mu\nu}$ is the density matrix element, and γ_{AB} is the two-center Coulomb integral. For basis orbitals on one center, $H_{\mu\nu} = 0$ and γ_{AB} is replaced by the one-center integral γ_{AA}. In method A, $K = 1$ for all matrix elements $F_{\mu\nu}$. In method, B, $K = 1$ is used for all the off-diagonal $F_{\mu\nu}$ elements except those connecting basis orbitals centered on the same second row atom, for which $K = {}^1\!/_2$. Adjusting particular one-center elements in this manner apparently improves the calculated dipole moments.[6]

The effect of this selective modification of matrix elements on the total energy is illustrated in Table I, which gives data for molecular chlorine, triplet state sulfur, and sulfur dioxide with different orientations in a Cartesian coordinate system. The variation of the energy is seen to be significant particularly for the diatomic molecules (*ca.* 0.8 and 0.3 kcal/deg for Cl_2 and S_2, respectively). An energy variation of this magnitude could lead to serious errors in, for example, the calculation of low rotational barriers. The lack of rotational invariance of method B clearly has its origin in the inequivalent handling of the γ_{AA} integrals in diagonal and off-diagonal Fock matrix elements while rotation of the axes causes off-diagonal density matrix elements $P_{\mu\nu}$ to be converted into $P_{\mu\mu}$ and $P_{\nu\nu}$ terms.[8]

Table I. Total Energies as a Function of Orientation by CNDO/2 Method B

	Energy, au		
θ, deg[a]	Cl_2[b]	S_2(triplet)[b]	SO_2[c]
0	−30.71320	−20.80310	−46.73545
30	−30.67738	−20.78797	−46.73627
45	−30.65403	−20.78018	−46.73656

[a] With the molecule in the *y,z* plane and one atom at the origin (S for SO_2), θ is the angle between the molecular axis (or SO bond) and the *z* axis. [b] Bond distance 2 Å. [c] S–O distance 1.5 Å, bond angle 90°

Invariance may be restored in method B by setting $K = 1$ uniformly for all off-diagonal Fock matrix elements.[9] Calculations then provide total energies

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(8) The diagonal Fock element is (ref 2) $F_{\mu\mu} = -\chi_\mu + [(P_{AA} - Z_A) - {}^1\!/_2(P_{\mu\mu} - 1)]\gamma_{AA} + \Sigma_{B(\neq A)}(P_{BB} - Z_B)\gamma_{AB}$, where χ_μ is the Mulliken-type atomic electronegativity, Z_A is the core atomic charge, and $P_{AA} = \Sigma P_{\mu\mu}$ (μ on A). *Cf.* J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, S129 (1965), for a discussion of transformation properties in CNDO theory.

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of −30.73070 (Cl_2), −20.83662 (S_2), and −46.76204 au (SO_2) for all the orientations listed in Table I. By comparison, method A gives a total energy of −21.99841 au for triplet state S_2 at all values of θ. Clearly, without the indicated modification, method B is unreliable for the theoretical investigation of molecular conformations and related problems.

Finally, we feel that attempts to improve second row CNDO theory are appropriate if it is to be widely used in theoretical investigations.

Acknowledgment. Partial support of this work by the donors of the Petroleum Research Fund administered by the American Chemical Society is gratefully acknowledged.

Partial Photoresolution. III.
The Tris(acetylacetonato)chromium(III) System

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Abstract: Tris(acetylacetonato)chromium(III) was partially resolved in circularly polarized light at 5461 Å in several organic solvents. The circular dichroism spectrum, normalized to that of pure enantiomer, yields a maximum at 420 nm and a minimum at 540 nm, with ($\epsilon_l - \epsilon_r$) having values of +1.7 and −4.3 M^{-1} cm^{-1}, respectively. Another maximum out of range of the CD machine occurs around 620–640 nm. Quantum yields for the photolytic inversion of enantiomers were measured in chlorobenzene solution as a function of wavelength and temperature. The results indicate that (1) the inversion is an order of magnitude less efficient than that of $Cr(C_2O_4)_3{}^{3-}$, (2) the photolysis is essentially wavelength independent in the visible region, and (3) the apparent activation energy is 2300 cal/mol at 5461 Å. Solvent studies indicate that the reaction is slightly more efficient in acetone and acetylacetone than in chlorobenzene, but that water inhibits the reaction slightly in acetone. A short discussion of mechanism is included.

Partial photoresolution, *i.e.*, the use of light in inducing optical activity in racemic mixtures through photolytic inversion of enantiomers, has been applied to several D_3 complexes of Cr(III) in aqueous solution.[1–3] When circularly polarized light is used, the degree of resolution is a direct function of the dissymmetry factor $g = (\epsilon_l - \epsilon_r)/\epsilon_{av}$, at the irradiating wavelength,[2] and hence such a partial resolution can be used to calculate the molar circular dichroism, $\epsilon_l - \epsilon_r$, without resorting to a complete, chemical resolution of optical isomers. Such experiments, coupled with photoracemization studies, can yield information about the photochemistry of the inversion process.

Tris(acetylacetonato)chromium(III) has been partially resolved[4] by column chromatography, most recently by Fay, *et al.*,[5] but the optical activity of pure enantiomer has not yet been determined. Moreover, its photochemistry in organic solvents might be expected to be different from that of Cr(III) complexes in aqueous solutions since the postulated mechanisms for the latter almost always involve water molecules. The purpose of this work, then, was (1) to determine the ORD and CD spectra of a pure enantiomer, and (2) to study the photolytic inversion of enantiomers in organic solvents through both photoresolution and photoracemization procedures.

Experimental Section

The complex, $Cr(acac)_3$, was prepared and purified according to established procedures.[6] *Anal.* Calcd for $Cr(C_5H_7O_2)_3$: C, 51.57; H, 6.06. Found: C, 51.66; H, 6.24.

Solutions of about 0.02 *M* were prepared and irradiated in constant-temperature cells made of glass or quartz thermostated to within 0.05° in an optical train described previously.[2] For photoracemization runs, the circular polarizer was removed from the train. At suitable time intervals the irradiation cell was transferred from the train to a Bendix Polarmatic 62 spectropolarimeter for ORD measurements. Twenty-five runs were made, and at the end of each the light intensity was measured using the potassium reineckate chemical actinometer.[7]

The solvents used were Spectroquality acetone, reagent grade chlorobenzene, and technical acetylacetone which had been triple distilled. None of the solutions were degassed because absorption spectra of irradiated samples were identical with those of fresh samples. Absorption spectra were taken on a Spectronic 505 spectrophotometer.

The circular dichroism spectrum of a partially resolved sample was made on a Cary 60 ORD-CD machine. A photoresolution run was made on trioxalatochromate(III) at 0° according to a previously described procedure[2] in order to determine its quantum yield for comparison purposes.

Results and Discussion

I. Optical Activity. The results of a 200-hr irradiation in circularly polarized, 5461 Å, light at 25° are shown in Figure 1. The parameter of optical activity observed was the difference between the maximum and minimum in the ORD Cotton effect curve, $\alpha_{max} - \alpha_{min}$. The steady-state optical activity has a slight positive slope because of small evaporation of solvent from the stoppered cell over long time periods. The

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