Conforrnational Studies of α-Substituted Carbonyl Cornpounds by the Molecular Orbital Method CNDO/2

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Abstract Within the framework of the CNDO/2 method, the energies and dipole moments computed as a function of a rotation angle are used to analyse the population ratios of cis and gauche conformers of five a--substituted acetones. The polar solvent effect is taken into account via a supermolecule model. UV and IR frequency shifts are discussed in terms of energy levels and hyperconjugation, respectively.

1. INTRODUCTION

Recently, Olivato[1] and coworkers have performed a systematic conformational analysis of some a-substituted acetones by IR measurements in solvents of increasing polarity and by UV measurements of the $n \to \pi^*$ carbonyl transitions in n-hexane. Their paper attempts to offer a qualitative explanation for both the relative stabilities of the cis and $gauche$ conformers and for the carbonyl frequency shifts of both rotamers in relation to the parent compound. Moreover, the energies of the $n \to \pi^*$ transitions of the carbonyl group are discussed as well as the corresponding band intensities.

In this paper we have attempted to discuss Olivato et al^1 conformational ratios and frequency shifts on more quantitative grounds using the molecular orbital method CNDO/2 as developed by Pople[2] and coworkers. Due to the parametrization restriction existent in the CNDO/2 version distributed by QCPE[3], only five a-substituted acetones, namely, fluoroacetone, chloroacetone, methoxyacetone, ethylthioacetone, and dimethylaminoacetone have been studied in this paper although experimental results are available for bromoacetone and iodoacetone also.

2. THE CALCULATION

With the exception of fluoroacetone[4], experimentally determined geometries were found for these molecules. In trying to use a consistent set of atomic coordinates for these molecules, the decision wasmade to use that geometry that minimizes the energy in the CNDO/2 approximation. Only interatonic distances considered as relevant were varied in this minimization process. They arethe carbon-oxygen distance in the carbonyl group, the carbon-heteroatom, and the carbon-carbon bonds. Standard tetrahedral (109.5°) and trigonal (120°) angles were employed were needed. Carbon-hydrogen bonds were set equal to 1.095 A. The calculated distances for the fluoroacetone for which experimental distances were found are: $R(C-C)$ = 1.46 Å (1.507 Å), $R(C=O)$ = 1.27 Å (1.222 Å), $R(C-F)$ = 1.35 Å (1.398 Å); the values in parenthesis are the experimental ones. Note that there is an error smaller than 4% in the calculated distances

Within two decimals precision the optimum values for the carbon-oxygen and carbon-carbon distances in the compounds were found to be the same as the ones quoted above. The other calculated distances are: Carbon-chlorine, 1.67 Å; carbon-nitrogen, 1.42 Å; carbon-oxygen (methoxy-group), 1.38 Å; and carbon-sulphur, 1.75 Å.

For the geometry given in Fig. 1, the energy and the dipole moment for every molecular species as a function of the rotation angle (ϕ) were computed and are graphically displayed in Figs. 2 and 3, respectively. In Fig. 2 the energy of the most stable conformer was chosen as the zero of energy, so that these curves can be seen as rotational barriers.
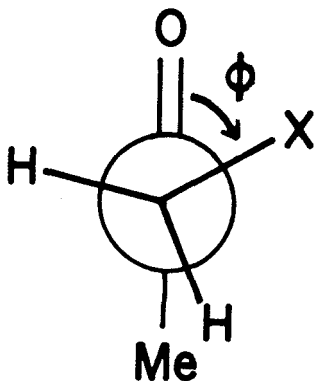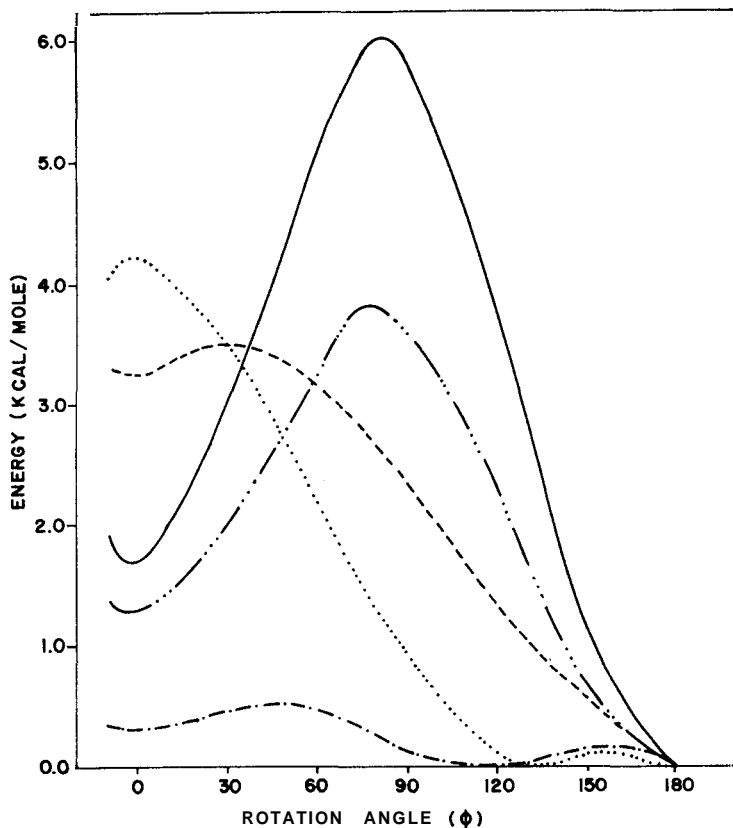

Fig.1 - The dihedral (rotation) angle ϕ.

Fig.2 – The energy as a function of the rotation angle:
—— fluoroacetone; --- chloroacetone; -·-·dimethylamino-
acetone; —··—·· rnethoxyacetone; ..... ethylthioacetone.

3. RESULTS AND DISCUSSION

A. Conforrnational analysis

The rotational barriers shown in Fig. 2 clearly indicate that the energetically favourable geometries are the ones corresponding to molecules in the gauche (trans) conforrnation. The curves for fluoro-acetone and methoxyacetone exhibit each two deep minima, the lowest one around 180° and the highest one around 0°. These minima are separated by relatively high barriers (about 6 kcal/mol for fluoroacetone and about 3.8 kcal/mol for methoxyacetone), The curve for ethylthioacetone shows a very wide minimum in the region $135^{o} < \phi < 215^{o}$, and a high maxi-
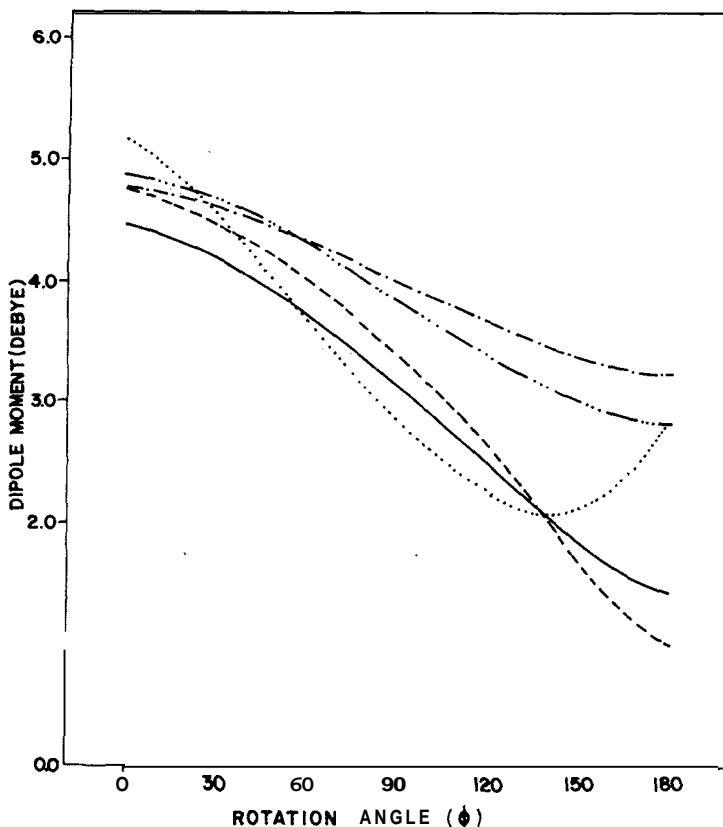
Fig. 3 - The dipole moment as a function of the rotation angle: —— fluoroacetone; --- chloroacetone; -·-· dimethylaminoacetone; -···— methoxyacetone; .... ethylthioacetone.

mum of about 4.2 kcal/mol around $\phi=0$. Notice in Table I that fluoroacetone (the highest barrier) and ethylthioacetone (high barrier and wide minimum) are the compounds with tne smallest (0.07) cis/gauche ratios. For chloroacetone, besides the global minimum at about $\phi=180^{\circ}$, only a very shallow and relatively high minimum around $\phi=0^{\circ}$ is predicted by the CNDO/2 calculation. The approximate nature of the molecular orbital approach being used makes it difficult to tell whetherthe non-existence of a more pronounced minimum around $\phi=0^{\circ}$ for the two compounds with second row elements (S, Cl) is a fact of nature or an artifact of the CNDO/2 method. Finally, dimethylaminoacetone shows the least energetic rotational barrier. Its height is only 0.5 kcal/mol, but its minimum

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Table 1 - Conformational population ratios of some α-substituted acetones.

| | CIS/GAUCHE RATIO | | |
	This work	Exp.[a]	Exp.[b]
Fluoroacetone	0.064	0.07	1.81
Chloroacetone	0.012	0,22	0.53
Dimethylaminoacetone	0.454	0.29	1.57
Ethylthioacetone	0.047	0.07	0.23
Methoxyacetone	0.105	0.19	1.86

[a] Non-polar solvent, n-hexane, Ref. (1). [b] Polar solvent, chloroform, Ref. (1).

extends practically from $\phi=115°$ to $\phi=245°$. This molecule shows the highest (0.29) cis/gauche ratio, but the *gauche* conformation is still the dominant one.

Experimentally, Olivato *et al*[1] defined a *cis/gauche* ratio as the ratio of the apparent molar absorptivities at the absorption maxima of the carbonyl stretching bands observed in the IR spectra. Can the *cis/gauche* ratio be inferred from our calculations? It is expected that the ratio of the probability of finding the molecule with an angle ϕ ranging from $0°$ to $90°$ over the probability of finding the molecule with an angle ϕ ranging from $90°$ to $\phi=180°$ can approximately give the observed ratios of Olivato et *al*[1]. This probability was estimated using the standard Boltzmann distribution

$$ P(\phi) = \int_{0}^{\phi1} \exp\left[-E(\phi)/kT\right]d\phi \bigg/ \int_{0}^{180} \exp\left[-E(\phi)/kT\right]d\phi $$

where, k is the Boltzmann constant, T the temperature, assumed equal to 300 K, and $E(\phi)$ is the energy as a function of the rotation angle ϕ as given in Fig. 2. An analytical expression for $E(\phi)$ was obtained using a least square fit, and the integrals were solved numerically. The calculated ratios are collected in Table 1, which also shows the experimental results of Olivato et *al*[1].

The quantitative agreement with experimental results is poor,

specially for chloroacetone, however the *gauche* conformation is predicted to be the preferred one in non-polar solvents, in qualitative agreement with the experimental trend. In the particular case of chloroacetone, this failure can certainly in part be attributed to parametrization problems in the CNDO/2 method. The overall results, however, may indicate that other factors besides free molecule rotation barrier must play an important role in the determination of the *cis–gauche* ratio.

In a polar solvent rhe experimental data show a reversion in the ratios for methoxyacetone, fluoroacetone, and dimethylaminoacetone, implying now a predominance of the cis conformation, while for chloroacetone and ethylthioacetone there is still a preference for the gauche conformation, although there has been an increase in the population of the cis conformer.

At first, one might be tempted to say that this reversion in the ratios can be attributed to the dipole-dipole interaction between solvent and solute. A glance at Fig. 3 shows, however, that all five species have about the same dipole moment at small values of the rotation angle. These data imply that the dipole-dipole interaction is certainly not the major effect responsible for the stabilization of the *cis* conformer relative to the *gauche* one.

The next step was to investigate how hydrogen bonding affects the stabilization of both conformers. Only hydrogen binding to the carbonyl oxygen was investigated, and fluoroacetone was taken as the prototype molecule. The approach used was the supermolecule method as extensively used by Pullmann[5] and coworkers. Essentially, one views the fluoroacetone and the chloroform molecule as a single unit forming a "supermolecule", as shown in Fig. 4.

The energy of the system is then calculated as a function of the angle a between the line joining the atoms C and H in the chloroform molecule, and the line joining the atoms C and O in fluoroacetone. Fig.5 shows this energy for both *cis* and *gauche* conformers and for the oxygen and hydrogen atoms 1.70 Å apart. The energy curve in Fig. 5 clearly indicates that cis conformation is energetically favoured when hydrogen bonding is taken into account. An energy minimum occurs at a $\sim 75^O$ for the *cis* conformer, and at a $\sim 85^O$ for the *gauche* one. Obviously, the carbonyl is not the only site for hydrogen bonding. The heteroatom can
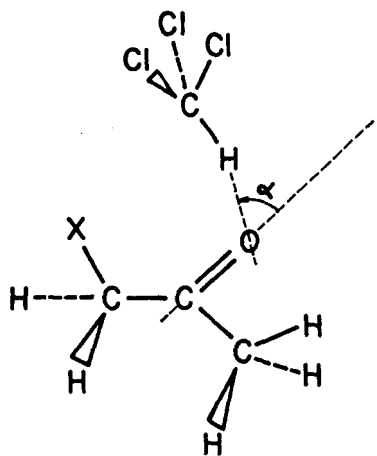
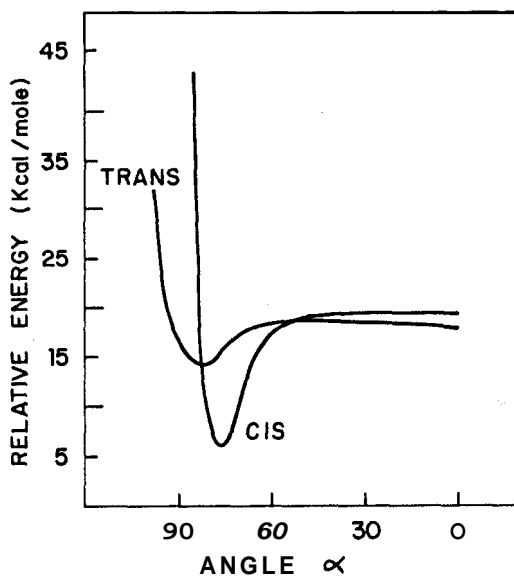Fig. 4 - The "supermolecule": α-substituted acetone-chloroform.

Fig.5 - Relative energies of the *cis* and *trans* conformers of the supermolecule fluoroacetone-chloroform.

also play such a role, and in fact the data in Table 1 seem to be consistent with the view that a second chloroform molecule is interacting via hydrogen bonding with the heteroatom. The stronger the binding the more stable the supermolecule, and it is a well known fact that the strength of a hydrogen bond is greater when 0, F and N atoms are involved in the binding, then when C1 and S are the atoms involved. Therefore, although a single chloroform molecule hydrogen bonded to the carbonyl oxygen stabilizes the *cis* conformer relative to the *gauche* one, it is certainly the strength of a second hydrogen bond involving the heteroatom that makes the *cis* conformer of the compounds containing the elements F, 0, and N much more stable than those involving C1 and S. And this is exactly the trend observed in Table 1.

B. Ultraviolet frequency shifts

Since the energies of two different electronic states should really be known in order to accurately obtain the transition frequency, and since this procedure is impratical for molecules of the size being studied, one frequently resorts to simple models where one hopes to predict at least the general trend of the shifts. One general practice is simply to calculate the difference in energies between the LUMO (π^*_{CO}) and the HOMO (n_0) [6]. If the Coulomb (J_{ij}) and exchange (K_{ij}) integrals over the molecular orbitals are available, the former difference can be corrected upon addition of the term $2K_{ik} - J_{ij}$ [7]. Even for this latter case, care must be taken in the conclusion since that formula is based on a frozen orbital single configuration description of the excited state, which is often inadequate. In Table 2 are listed the experimentally observed $n \rightarrow \pi^*$ frequencies[■] and estimates based on the two approaches mentioned above.   ,

The differences in energies of the LUMO and HOMO are indicative that for fluoroacetone, methoxyacetone and chloroacetone there should be a red shift relative to acetone, whereas for dimethylaminoacetone and ethylthioacetone there should be a blue shift.   The blue shift conclusion although in direct conflict with the experimental data is in complete agreement with earlier calculation of Allinger et *al*[8] on ciclohexanones. These authors have concluded that the red shift induced in ciclohexanone $n \rightarrow \pi^*$ transition by axial halogen substituents

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Table 2 - Experimental $n \to \pi^*$ transition energies and estimates based on CNDO/2 method.

	ν_{max}^{**}/cm^{-1}	ΔE^+/cm^{-1}	ΔE^{++}/cm^{-1}
pentan-2-one	35,842	135,152*	44,393*
fluoroacetone	35,714	134,011	44,266
methoxyacetone	35,335	133,001	45,915
dimethylaminoacetone	34,364	139,168	
chloroacetone	34,364	130,982	59,142
ethylthioacetone	33,222	137,961	

* Calculations done for acetone. ** Experimental Ref. 1. $^+$ $\Delta E = \varepsilon_j - \varepsilon_i$. See text. $^{++}$ $\Delta E = \varepsilon_j - \varepsilon_i - J_{ij} + 2K_{ij}$. See text.

is due to an interaction between the carbonyl π_{CO}^* orbital and the a_{C-x}^* orbital, with a consequent lowering of the π_{CO}^* energy level. This should happen if either X is electronegative (σ_{C-x}^* lower in energy) or if the bond is weak, so that the a and σ^* energy levels are not very far apart In Fig. 6 as a function of the rotation angle ϕ are plotted the energy levelsof the π_{CO}^*, n_0 and π_{CO} orbitals. These curves exactly reflect Allinger's et al[8] conclusion. For fluoroacetone, methoxyacetone, and chloroacetone there is a lowering of the π_{CO}^* energy level, and for dimethyl-aminoacetone and ethylthioacetone there is a raising of the π_{CO}^* level. We recall that in the Pauling scale, the electronegativities For the heteroatoms are: F (3.98), O (3.441, Cl (3.16), N (3.04), S (2.58) and H (2.20). The results discussed above seem to indicate that conclusions about red or blue shifts based on the lowering or raising of orbital energy levels calculated for the molecule in the ground state çhould be taken with reserve, specially if approximate methods are involved. The experimental results for dimethylaminoacetone and ethylthioacetone clearly cannot be explained by the approximate model invoked here.

C. Carbonyl stretching frequency shifts

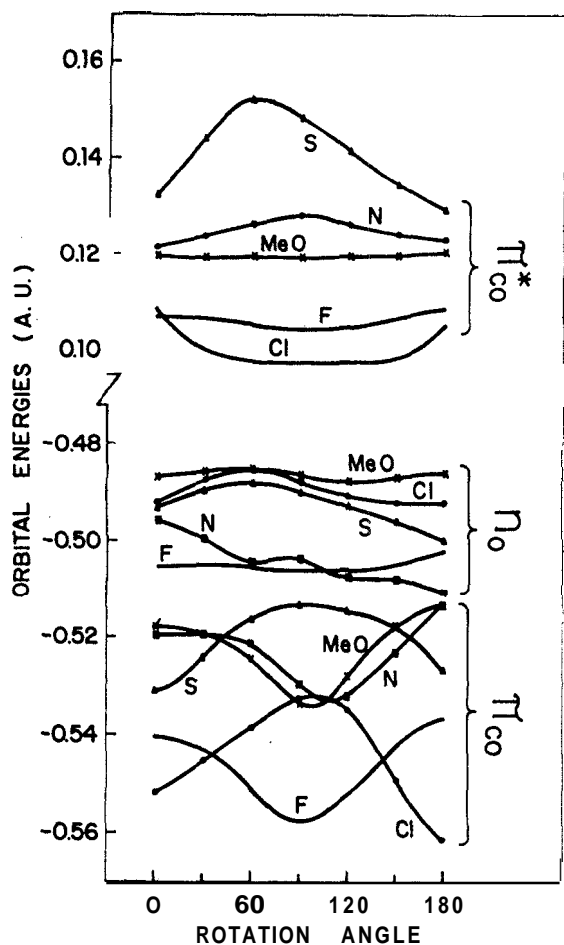A thorough discussion of the different effects that rnight be

Fig.6 - Orbital energies as a function of the rotation angle,

involved in the carbonyl stretching frequency shifts in the species considered here has been done by Olivato et al^{1}. In this section we want to complement his view of a hyperconjugative interaction using information obtained from the molecular orbital calculation.

In Table 3 we have summarized the populations of the 2p atomic orbitals of the carbonyl carbon (π_{c}) and carbonyl oxygen (π_{0}), and also the charge on the oxygen (Q_{0}) for several dihedral angles. There is also a A value included which represents the variations of the populations of the $2p\pi$ atomic orbitals on the carbonyl oxygen and carbonyl carbon in comparison with the corresponding orbitals in fluoroacetone which was taken as the reference compound.

Table 3 - Populations of the 2pπ atomic orbitals of the carbonyl carbon and oxygen atoms (π_c, π_0) and the charge (Q_0) on the carbonyl oxygen (in units of 10^{-3} electrons).

Degree		S	Cl	N	O	F
0°	π_c	0.807	0.817	0.814	0.817	0.823
	π_0	1.274	1.263	1.268	1.262	1.256
	Δ^a	2	3	1	0	0
	Q_0	238	269	279	270	258
90°	π_c	0.797	0.814	0.805	0.818	0.833
	π_0	1.308	1.272	1.278	1.252	1.227
	Δ^a	45	26	23	10	0
	Q_0	308	280	287	272	254
120°	π_c	0.798	0.811	0.808	0.808	0.826
	π_0	1.302	1.273	1.273	1.257	1.240
	Δ^a	34	18	15	6	0
	Q_0	305	281	261	275	286
150°	π_c	0.798	0.805	0.809	0.809	0.814
	π_0	1.294	1.282	1.275	1.273	1.267
	Δ^a	11	6	3	1	0
	Q_0	301	286	289	285	275
180°	π_c	0.797	0.801	0.810	0.805	0.808
	π_0	1.292	1.291	1.277	1.282	1.280
	Δ	1	4	1	1	0
	Q_0	300	292	291	290	283

$^a = |\pi_0(x) - \pi_0(F)| - |\pi_c(x) - \pi_c(F)|$, $x = S, Cl, N, O, F$

One can notice in Table 3 that for the *cis* and *trans* conformerç the decrease in population of the 2pπ atomic orbitals on the carbonyl carbon relative to fluoroacetone along the series F, O, N, Cl, S is approximately equal to the increase in the 2pπ atomic orbital population on the carbonyl oxygen. But, one can also notice that as the dihedral angle changes to 150°, 120° and 90°, the decreases in population of the

$2p\pi$ atomic orbitals on the carbonyl carbon is less than the corresponding increases in the population of the $2p\pi$ atomic orbitals on the carbonyl oxygen. This fact, as discussed by Pople[9], is indicative of a transfer of a-electrons from the CH_2-X group into the carbonyl groupby hyperconjugation. This electron transfer is maximum at 90°, and is also more prominent for the S and C1 compounds, and practically inexistent for fluoroacetone. It is noteworthy that this result is well in accord with the estimates of Olivato et al^1 for the frequency shifts (in cm^{-1}) of the carbonyl group due to the hyperconjugation effect $(\Delta\nu_H)$ which follows the order F (0.0), O(-2.1), N (-4.2), C1 (-8.1) and S (-15.5).

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Resumo

Através da parametrização do método CNDO/2 foi possível analisar a população relativa dos confôrmeros *cis* e gauche de 5 acetonas α -heterossubstituídas, através do cálculo das energias e dos momentos dipolares em função do ângulo de rotação ϕ. O efeito do solvente foi estimado via o modelo de uma supermolécula e os deslocamentos de frequência tanto no U.V. quanto no I.V. são discutidos em termos dos níveis deenergia e da hiperconjugação respectivamente.