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Barriers to Molecular Inversion in $(n\pi^*)$ Carbonyls: A CNDO Investigation

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CNDO/2 calculations performed on a series of carbonyl-containing compounds have shown that inductive effects by electronegative substituents with respect to hydrogen play the major role in determining the height of the inversion barrier relative to formaldehyde. The change in density flow at the central carbon atom for different carbonyl substituents parallels the calculated inversion barriers in accordance with Walsh's rules.

Mit Hilfe von CNDO/2-Rechnungen wurde für eine Reihe von Verbindungen mit Carbonylgruppen gezeigt, daß die Höhe der Inversionsbarriere relativ zu Formaldehyd vorwiegend durch induktive Effekte der elektronegativen Substituenten in bezug auf Wasserstoff bestimmt wird. Die Ladungsflußänderungen am zentralen Kohlenstoffatom entsprechen in Übereinstimmung mit den Walshschen Regeln den berechneten Inversionsbarrieren.

Des calculs CNDO/2 effectués sur une série de composés carbonylés ont montré que les effets inductifs dûs à des substituants électronégatifs par rapport à l'hydrogène jouent un rôle essentiel dans la détermination de la hauteur de la barrière d'inversion par rapport au formaldéhyde. Les variations de transfert de charge sur l'atome de carbone central selon les différents substituants carbonylés sont parallèles aux barrières d'inversion calculées en accord avec les règles de Walsh.

Introduction

During the past several years optical spectroscopists have studied the electronic transitions from the ground electronic state to the first $^1n\pi^*$ states of simple aldehydes and ketones such as formaldehyde [1], formyl fluoride [2], propynal [3], phosgene [4], and cyclobutanone [5]. While infrared and microwave studies have established that these molecules are planar in the ground electronic state, evidence has been provided to show that the excited state structures of these molecules are pyramidal. One interesting observation that can be made when looking at the excited state structures is that there is a great variation in the barrier heights to molecular inversion. For example, the inversion barrier for propynal is close to $0\,\mathrm{cm}^{-1}$, whereas for H_2CO it is $356\,\mathrm{cm}^{-1}$ and for Cl_2CO it is $3170\,\mathrm{cm}^{-1}$. It appears, then, that the barrier to inversion is very sensitive to the type of substituent on the carbonyl group.

In view of the success of the CNDO method developed by Pople, Santry, and Segal [6] in the calculation of a number of properties of simple polyatomic molecules, we thought that we could use it to obtain an understanding of the role that the substituents play in determining the height of the inversion barrier.

Calculations

For the ground state and for the first triplet state, CNDO/2 calculations were performed for the molecules F_2CO, HFCO, H_2CO, C_4H_6O (cyclobutanone), CH_3CHO, and HCCCHO. The CNDO/2 program as introduced by Pople and Segal [7] was not modified for our purposes. The out-of-plane angle, which is defined as the angle between the C=O bond and the projection of the C=O bond onto the molecular plane, was varied in each calculation, while the XCY angle (where C is the carbonyl carbon atom and X and Y are the substituents) and the C=O bond length were clamped at their ground state values throughout the inversion process. While Kroto and Santry [8] have demonstrated, through calculations on the formaldehyde molecule, that the barrier is sensitive to the choice of inversion coordinate, we felt that this procedure was acceptable, since we were concerned only with the relative barriers to inversion. The geometries used in the calculations for the molecular series $F_2CO/HFCO/H_2CO/C_4H_6O/CH_3CHO/$ HCCCHO are found in references [9] to [14] respectively.

Results and Discussion

Table 1 presents the calculated barrier heights and out-of-plane angles for the molecules studied, along with the experimental values for comparison purposes. It is evident that the CNDO method is successful in predicting the relative order of the barrier heights to molecular inversion, with the exception of cyclobutanone. A direct comparison of the calculated and experimental data should not be made, though, since the calculated data refer to the triplet excited state, while the experimental data refer to the corresponding singlet state. For planar $n\pi^*$ states, however, the exchange integral vanishes in the CNDO approximation, and the two states become degenerate [15].

To obtain an insight into the factors responsible for the variation in barrier with change in carbonyl substituent, we attempted to extend Walsh's rules to the series of substituted carbonyl compounds. In 1953 Walsh [16] qualitatively

Table 1. Calculated and experimental barriers to inversion and out-of-plane angles for the $(n\pi^*)$ states of some carbonyl compounds

Molecule	Barrier (cm^{-1})		Angle (degrees)		Ref.
	expt.[a]	calc.[b]	expt.[a]	calc.[b]	
F_2CO	>4000	4600	—	40	[19]
HFCO	2800–4200	1900	30–35	38	[2]
H_2CO[c]	356	760	33.6	35	[20]
C_4H_6O	1550	180	—	23	[5]
CH_3CHO	—	50	—	18	
HCCCHO	~0	0	0–4	0	[21]

[a] For the $^1(n\pi^*)$ state.

[b] For the $^3(n\pi^*)$ state.

[c] A value of 776 cm^{-1} has been calculated [20] from the observed inversion levels of $^3A_2$ H_2CO.

Table 2. Electron densities at the C=O group

Molecule	Atom	Ground state				Planar excited state				Non-planar excited state			
		$2s$	$2p_x$	$2p_y$	$2p_z$	$2s$	$2p_x$	$2p_y$	$2p_z$	$2s$	$2p_x$	$2p_y$	$2p_z$
F_2CO	C	0.9950	0.7791	0.7344	0.8299	0.9208	1.2548	0.7357	0.7471	1.1101	0.9984	0.7370	0.7714
	O	1.7144	1.3631	1.8841	1.3118	1.7251	1.8410	1.0105	1.4607	1.7298	1.6604	1.0172	1.6417
HFCO	C	1.0394	0.8211	0.8273	0.8828	0.9897	1.2457	0.8322	0.7923	1.1227	1.0497	0.8322	0.8123
	O	1.7202	1.2419	1.9065	1.3584	1.7308	1.7990	1.0525	1.4646	1.7323	1.6517	1.0620	1.6021
H_2CO	C	1.0888	0.8358	0.9321	0.9245	1.0505	1.2356	0.9298	0.8467	1.1389	1.0858	0.9271	0.8794
	O	1.7281	1.1642	1.9188	1.3738	1.7364	1.7644	1.0833	1.4610	1.7371	1.6443	1.0945	1.5703
C_4H_6O	C	1.0175	0.8183	1.0363	0.8728	0.9719	1.1919	1.0203	0.7914	1.0222	1.1177	1.0176	0.8106
	O	1.7357	1.2415	1.9425	1.3391	1.7438	1.8019	1.1082	1.4453	1.7444	1.7295	1.1110	1.5172
CH_3CHO	C	1.0429	0.8258	0.9569	0.9244	1.0049	1.2063	0.9509	0.8399	1.0249	1.1603	0.9675	0.8435
	O	1.7318	1.2118	1.9367	1.3506	1.7406	1.7947	1.0806	1.4540	1.7408	1.7686	1.1053	1.4558
HCCCHO	C	1.0219	0.8385	0.9623	0.9165	0.9897	1.1737	0.9640	0.8416				
	O	1.7312	1.1936	1.9368	1.3497	1.7393	1.7899	1.0786	1.4479				

correlated molecular geometry and orbital energy for a variety of molecules. For H_2CO, the Walsh diagram correctly predicts a non-planar excited state equilibrium structure. The main principle on which he based his correlation is the following: whether or not an orbital becomes more tightly bound with change of angle is determined primarily by whether or not it changes from being built from a *p* orbital on an atom to being built from an *s* orbital on that atom. The *s* and *p* orbital character at each atomic center is given by the elements of the CNDO density matrix. An interpretation of the CNDO density matrices for the ground and excited electronic states of the series F_2CO/HFCO/H_2CO/C_4H_6O/CH_3CHO/HCCCHO from the viewpoint of the Walsh postulate should provide information about the non-planarity of the upper state. Table 2 compares the electron densities at the carbonyl group for each of the molecules studied in their ground, planar excited, and non-planar excited states. For the planar configurations the coordinate axes were set up such that the C=O bond is parallel to the z axis, and the x axis is perpendicular to the molecular plane. In the calculations on the non-planar configurations, the XCY framework was taken to be in the yz plane.

In a $\pi^* \leftarrow n$ electronic transition, an electron is promoted from a filled n orbital to a previously unoccupied π^* orbital. The electron densities listed in Table 2 for the carbonyl group illustrates this clearly, in that for H_2CO, the n orbital on oxygen $[2p_y(\mathrm{O})]$ has a density of 1.9188 for the $^1A_1$ state, while for the $^1A_2$ state it takes a value of 1.0833. The ground state density in the π orbital for the carbon and oxygen atoms is given respectively as 0.8358 and 1.1642. The corresponding densities for the excited electronic state are 1.2356 and 1.7644. The loss in density for the n orbital is therefore -0.8355, while the gain in density in the x direction for carbon and oxygen is, respectively, 0.3998 and 0.6002. These density differences for the series of molecules studied are given in Δ_1 of Table 3. The Δ_2 values in this table are the differences in electron densities which result from a transition from the ground state to a non-planar excited state, and were obtained from the first and third sets of data listed in Table 2. $\Delta_2 - \Delta_1$, then, gives the difference in electron density between the non-planar and planar excited states.

Table 3. Density differences

Molecule	Atom	Δ_1				Δ_2				$\Delta_2 - \Delta_1$			
		$2s$	$2p_x$	$2p_y$	$2p_z$	$2s$	$2p_x$	$2p_y$	$2p_z$	$2s$	$2p_x$	$2p_y$	$2p_z$
F_2CO	C	-0.0742	0.4757	0.0013	-0.0828	0.1151	0.2193	0.0026	-0.0585	0.1893	-0.2564	0.0013	0.0243
	O	0.0107	0.4779	-0.8736	0.1489	0.0154	0.2973	-0.8679	0.3299	0.0047	-0.1806	0.0057	0.1810
HFCO	C	-0.0497	0.4246	0.0049	-0.0905	0.0833	0.2286	0.0049	-0.0705	0.1330	-0.1960	0.0000	0.0200
	O	0.0106	0.5571	-0.8540	0.1062	0.0121	0.4098	-0.8445	0.2437	0.0015	-0.1473	0.0095	0.1375
H_2CO	C	-0.0383	0.3998	-0.0023	-0.0778	0.0501	0.2500	-0.0050	-0.0451	0.0884	-0.1498	-0.0027	0.0327
	O	0.0083	0.6002	-0.8355	0.0880	0.0090	0.4801	-0.8243	0.1973	0.0007	-0.1201	0.0112	0.1039
C_4H_6O	C	-0.0456	0.3736	-0.0160	-0.0814	-0.0047	0.3014	-0.0187	-0.0622	0.0409	-0.0722	-0.0027	0.0192
	O	0.0081	0.5604	-0.8343	0.1026	0.0087	0.4880	-0.8315	0.1781	0.0006	-0.0724	0.0028	0.0755
CH_3CHO	C	-0.0380	0.3805	-0.0060	-0.0845	-0.0180	0.3345	0.0131	-0.0809	0.0200	-0.0460	0.0191	0.0036
	O	0.0088	0.5829	-0.8561	0.1034	0.0090	0.5568	-0.8314	0.1052	0.0002	-0.0261	0.0247	0.0018
HCCCHO	C	-0.0322	0.3352	0.0017	-0.0749								
	O	0.0081	0.5963	-0.8582	0.0982								

For H_2CO, the $\Delta_2 - \Delta_1$ values for the $2p_x$(C) orbital and the $2s$(C) orbital are, respectively, -0.1498 and 0.0884. That is, when planar formaldehyde in the $n\pi^*$ configuration is distorted from the plane by 35°, there is a shift in electron density away from the $2p_x$ orbital on the carbon atom into the $2s$ orbital. This is in agreement with the Walsh postulate, in that a gain in s density leads to a more stable configuration, which in the case of H_2CO corresponds to a non-planar structure. Since Walsh's rule states that the degree of non-planarity in the $n\pi^*$ states depends upon the amount of s character acquired by the π^* orbital, the height of the inversion barrier should then parallel the $2p_x$ and $2s$ density changes at the carbonyl carbon atom. Hence, it should be possible to establish a correlation between the $\Delta_2 - \Delta_1$ values and the inversion barriers for the series of molecules studied. From Table 3, $\Delta_2 - \Delta_1$ values for the $2p_x$ orbital for the molecular series F_2CO/HFCO/H_2CO/C_4H_6O/CH_3CHO/HCCCHO are, respectively, -0.2564, -0.1960, -0.1498, -0.0722, -0.0460, and 0. The corresponding gain in carbon $2s$ electron density for the same series is 0.1893, 0.1330, 0.0884, 0.0409, 0.0200, and 0.

The orbitals on the oxygen atom also show significant density changes. The $\Delta_2 - \Delta_1$ values for the $2p_x$(O) orbital for the series are -0.1806, -0.1473, -0.1201, -0.0724, -0.0261, and 0. The corresponding gain in the oxygen $(2s + 2p_z)$ density is 0.1857, 0.1390, 0.1100, 0.0749, 0.0020, and 0, with nearly all of this density going into the $2p_z$ orbital. This indicates that density flow on the oxygen atom, as on the carbon atom, is in the direction from the π to the σ framework.

Brundle *et al.* [17] have recently demonstrated in a photoelectron study of H_2CO and F_2CO that the effect of substitution of fluorine for hydrogen has a much larger stabilization effect on the σ MO's than on the π MO's. Therefore, the $2p_x$(C) AO which goes to form the π MO is relatively unaffected by substitution on the carbonyl group. The σ MO's in these compounds belong to the representations A_1 and B_2, while the π MO belongs to the B_1 representation. When the molecule is distorted from the planar (C_{2v}) to the non-planar (C_s) form, the A_1 and B_1 representations correlate with A', and the A_2 and B_2 representations correlate with A''. Therefore, in a non-planar system, the $\sigma - \pi$ distinction is no longer valid, and it follows that the $2p_x$(C) orbital can be perturbed by an electronegative substituent. In the case of F_2CO, the carbon $2p_x$ AO responds to fluorine induction, with the result that there is a net charge flow from the $2p_x$(C) into the $2s$(C) AO. From the viewpoint of the Walsh postulate, a change in electron density in this direction would result in a non-planar distortion at the carbon center. The height of the inversion barrier and the out-of-plane angle can be considered, then, to result from an inductive effect of the attached group.

In the case of propynal, the π and π^* orbitals are delocalized over four atomic centers, and consequently the necessity for a density flow from the $2p_x$(C) to the $2s$(C) AO is reduced. Both the calculated and observed barrier heights for propynal reflect this. The lack of agreement in the data for cyclobutanone may be attributed to molecular strain arising from the four-membered ring. For the case of inverting nitrogen heterocycles [18], however, this deficiency has been overcome by a reparametrization of the CNDO electronegativities.

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