$^{1,3}(n-\pi^*)$ excited states of benzaldehyde

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Abstract. Geometries of the first triplet and first singlet $n-\pi^*$ excited states of benzaldehyde have been optimized using the SINDO 1 molecular orbital wave-function (with CI) and the Newton–Raphson method. The triplet excited state geometry of the molecule is found to be appreciably non-planar whereas that of the singlet excited state is planar. A crossing of molecular orbitals occurs in going from the ground state equilibrium geometry to the triplet and singlet $n-\pi^*$ excited state equilibrium geometries. Existence of the para-directing effect of the singlet $n-\pi^*$ transition for electronic charges found in an earlier work is confirmed by the present work. The triplet $n-\pi^*$ excitation rearranges electronic charges mainly on the CHO group. It is found that the dipole moment of the molecule would appreciably increase following the singlet $n-\pi^*$ excitation whereas the same would appreciably decrease following the triplet $n-\pi^*$ excitation.

1. Introduction

Though broad features of the electronic spectrum of benzaldehyde are fairly well understood (Haque 1979), several important aspects such as excited state geometry, excited state dipole moment, origin of the differences between the photochemical behaviours of the singlet and triplet $n-\pi^*$ excited states are not understood properly. For example, Hollas and Thakur (1973) from the study of fluorescence spectrum of benzaldehyde concluded that this molecule has a planar geometry in the excited singlet $n-\pi^*$ state. Koyanagi and Goodman (1971, 1979) concluded that benzaldehyde in the first triplet $n-\pi^*$ excited state is planar in a closed-packed matrix but strongly non-planar (angle of twist of CHO group $\sim 60°$) in a relaxed matrix or in its free state. It is not clear why there should be such a strong effect of the matrix environment on the triplet excited state molecular geometry. In a recent molecular orbital calculation on a number of conjugated ring molecules with n electrons, it has been found that singlet $n-\pi^*$ transitions direct electronic charges to the para-position of a pyridine type nitrogen situated on the ring or to the para-position of the ring atom to which an external CHO group is attached (Tewari and Mishra 1984). It is not clear whether a similar situation exists in triplet $n-\pi^*$ states also. Further, the singlet $n-\pi^*$ excited state dipole moment of benzaldehyde has been shown to be larger than the ground state value in another work (Srivastava and Mishra 1980). This question with regard to the triplet excited state has not been studied. The conclusions obtained for singlet $n-\pi^*$ excited states are not expected to be applicable to the triplet states since their

photochemical properties are known to be quite different. These questions related to benzaldehyde have been studied in this work using a reliable molecular orbital method and geometry optimization.

2. Method of calculation

The SINDO 1 molecular orbital method which has been shown to be satisfactory for ground and excited state properties as well as for reactions of a variety of molecules was used for the calculations (Jug and Nanda 1980; Mishra and Jug 1982; Muller–Remmers *et al* 1984; Nanda and Jug 1980). The SINDO 1 method involves modifications over the INDO method with regard to the evaluation of core-Hamiltonian matrix elements over orthogonalized atomic orbitals, introduction of a pseudo-potential term to incorporate inner-shell outer-shell repulsion, introduction of a so-called anti-penetration factor to avoid excessive binding (as obtained in CNDO/1), modification of orbital exponents, etc. Details of the SINDO 1 method are available elsewhere (Jug and Nanda 1980; Nanda and Jug 1980). The Newton–Raphson method was used to search energy minima (Himmelblau 1972). Several low lying configurations which were constructed with SCF molecular orbitals were included in the configuration interaction calculations. The ring was considered to be hexagonal with 1·419 Å CC bond lengths in the ground as well as excited states while the geometry of the CHO fragment was optimized in all the states. This was considered to be sufficient to obtain the qualitative features of charge redistribution consequent to excitation of the molecule and geometry of the CHO fragment.

3. Results and discussion

3.1 *Molecular geometry*

Geometry of the CHO group in the ground and excited states is given in table 1. All the internal coordinates are different in the various states though appreciable differences are observed only for a few. Elongation of the CO bond is very small in the triplet $n-\pi^*$ excited state whereas it is significant in the singlet $n-\pi^*$ excited state. The reverse trend is observed for the CH and ring–CHO bond lengths. The OCH bond angle is close to 120° in the ground and triplet excited states whereas it is appreciably opened in the singlet excited state. In the triplet excited state, the CHO group is non-planar as described below. The C_1 CO and C_1 CH planes are twisted with respect to the ring plane by about 27·5° and 9° respectively. The carbon atom of the CHO group lies about 0·01 Å above the ring plane whereas the hydrogen and oxygen atoms lie below the plane by about 0·15 and 0·46 Å respectively. In the singlet excited state, the geometry of the CHO group is planar as it is in the ground state. This situation is very similar to that found in formaldehyde (Mishra and Jug 1982). The SINDO1 method predicts formaldehyde also to be planar in the singlet $n-\pi^*$ excited state and non-planar by about 27·5° in the triplet $n-\pi^*$ excited state (Mishra and Jug 1982). *Ab initio* calculations show that formaldehyde is more non-planar in the triplet $n-\pi^*$ excited state than in the singlet $n-\pi^*$ excited state (Buenker and Peyerimhoff 1978). Further, the potential curve of the singlet $n-\pi^*$ excited state of formaldehyde corresponding to variations in non-planarity is very

Table 1. Geometry of the CHO group of benzaldehyde.

Coordinate*	Values (A and degrees)		
	Ground state	Triplet $n\text{-}\pi^*$ excited state	Singlet $n\text{-}\pi^*$ excited state
CO	1·211	1·217	1·232
CH	1·091	1·097	1·077
C_1C	1·555	1·558	1·543
OCH	120·2	120·0	130·4
C_1CO	125·9	121·0	124·6
C_1CH	113·9	107·7	105·5
C_2C_1C	121·0	122·0	123·6
C_6C_1C	119·0	118·0	116·4
$C_3C_2C_1C$	180·0	181·0	180·0
C_2C_1CH	180·0	189·0	180·0
C_2C_1CO	0·0	−27·5	0·0

* The ring atom bonded to the CHO group is designated as C_1 while others are designated as C_2 to C_6 sequentially in a clockwise sense C_2 lies on the same side as O.

flat (Mishra and Jug 1982; Buenker and Peyerimhoff 1978). The similarities between the benzaldehyde and formaldehyde $n\text{-}\pi^*$ excited states suggest that benzaldehyde may also be somewhat non-planar in the singlet $n\text{-}\pi^*$ excited state but the corresponding potential surface would be quite flat due to which detecting the non-planarity or its effects would be difficult.

On the basis of these considerations we can explain the experimental observations on benzaldehyde. First, the conclusion of Hollas and Thakur (1973) that benzaldehyde is planar in the singlet $n\text{-}\pi^*$ excited state is quite genuine. Second, the conclusion of Koyanagi *et al* (1971, 1979) that this molecule is non-planar in the triplet $n\text{-}\pi^*$ excited state is also acceptable. The reason for a large change in non-planarity of the $n\text{-}\pi^*$ triplet excited state geometry of benzaldehyde under the change of host matrix may be understood in terms of flatness of the potential surface corresponding to variation in non-planarity. For formaldehyde the $n\text{-}\pi^*$ triplet excited state energy rise in going from the equilibrium non-planar to the planar geometry is less than 0·1 eV (Buenker and Peyerimhoff 1978). We may assume the same to be qualitatively true for benzaldehyde also. A close packing in a host matrix may raise the energy of any state of the molecule by this amount; consequently the molecule will be found to be planar in such a matrix. However, on the basis of our calculations it appears that non-planarity of benzaldehyde for the CHO group in the triplet $n\text{-}\pi^*$ excited state (60°) as suggested by Koyanagi *et al* (1971, 1979) is overestimated.

3.2 *Nature of transitions and molecular orbitals*

We can analyse the qualitative aspects of the transitions and their relationship with relaxation of the CHO geometry. The orbitals may be numbered in the increasing order of energy. When this is done, the ground state orbitals 18 (π), 19 (n), 22 (σ^*) and 23 (π^*)

correlate respectively with those of both the singlet and triplet $n-\pi^*$ excited state equilibrium geometries and numbered as $19(\pi)$, $18(n)$, $23(\sigma^*)$ and $22(\pi^*)$. The designations π and σ are approximate for the triplet excited state. Thus in going from the ground state to both the excited states, the orbitals $18(\pi)$ and $19(n)$ and similarly $22(\sigma^*)$ and $23(\pi^*)$ cross. While the $18(n)$ to $21(\pi^*)$ excitation is entirely responsible for the singlet $n-\pi^*$ state in its equilibrium geometry, $18(n)$ to $21(\pi^*)$ and $20(\pi)$ to $23(\sigma^*)$ both contribute significantly (about 70% and 30% respectively) to the triplet $n-\pi^*$ excited state in its equilibrium geometry. In the ground and singlet excited states, the n orbital is found to be strongly localized on the CHO group whereas in the triplet excited state the localization is somewhat less due to the non-planar molecular geometry in this state. Thus the present SINDO 1 calculation supports the assignment of the non-bonding orbital as a genuine one; it was established in an earlier CNDO–S/CI calculations (Srivastava and Mishra 1980), but was made doubtful due to the work of another group (Hollas et al 1970). Since we are keeping the six-membered ring geometry fixed, we cannot expect to obtain accurate values of excitation energies from our calculations as differences of ground and excited state total energies. An examination of the relevant orbitals shows that transitions would cause shortening of the C_2C_3 and C_5C_6 ring bonds (C_1 being bonded to the CHO group) and elongation of the other four CC ring bonds. Our CNDO–S/CI calculation also predicts the same feature. This effect is much more in the singlet excited state than in the triplet excited state accordingly. It may also be understood with the help of excited state charge distributions discussed in the next section which show that the effect of singlet excitation on the ring is more pronounced than that of the triplet excitation. In other words, ring geometry would undergo larger change consequent to the singlet excitation than due to the triplet excitation. Therefore, one would expect a larger calculated singlet-triplet splitting than the experimental value of 0.25 eV. The present calculation yields 0.26, 0.9 and 1.44 eV for the $n-\pi^*$ singlet-triplet separations as found vertically below the singlet surface minimum, total energy difference of the two states and vertically above the triplet state minimum. This situation arises due to the fact that the singlet and triplet state energy minima have different locations on the multi-dimensional potential surface. At the present level of optimization the calculated excitation energies are appreciably larger than the experimental values (Haque 1979): triplet 3.15 eV; singlet 3.40 eV. Improvement in this regard would be obtained on optimization of the ring geometry. But it was not necessary since our main objectives are reasonably met even otherwise.

3.3 Charge distribution and dipole moment

As mentioned earlier, from the previous studies on benzaldehyde and other molecules containing n-electrons, it has been shown that singlet $n-\pi^*$ transitions have a para-directing effect for electronic charges and that the $n-\pi^*$ excited singlet state dipole moment is larger than the ground state value. While on one hand the present SINDO 1 study confirms these findings, on the other it also sheds light on the differences between the singlet and triplet $n-\pi^*$ excited states.

Rearrangements of charges following the singlet and triplet $n-\pi^*$ excitations of benzaldehyde have been presented in figures 1. We find that consequent to both the excitations, oxygen and hydrogen atoms of the CHO group lose electronic charges appreciably and this loss is larger in the singlet state than in the triplet state. In the singlet $n-\pi^*$ excited state the electronic charges are mainly concentrated at the para-
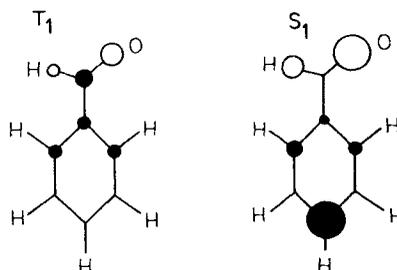
Figure 1. Rearrangement of charges in going from the ground to the first triplet and first singlet $n\text{-}\pi^*$ excited states. Change of 0·04 electronic charge has been taken to be equivalent to a circle of 1 mm radius. The open circles show loss of electronic charge while the closed ones gain of electronic charge.

position to the carbon atoms C_1 *i.e.* at C_4 although small gains of electronic charges are also made by the atoms C_2 and C_6. It is also interesting to note that gain of the electronic charges following the singlet $n\text{-}\pi^*$ excitation by the carbon atom C_4 is almost equal to the loss of electronic charges by the oxygen atom. The charge distribution in the triplet $n\text{-}\pi^*$ excited state differs from that of the singlet $n\text{-}\pi^*$ excited state mainly in one respect. That is, in the triplet excited state the electronic charges mainly concentrate at the carbon atom of the CHO group; only small gains of electronic charges are made by the carbon atoms C_2 and C_6 as in the singlet excited state. Thus the para-directing effect for electronic charges which holds good for the singlet $n\text{-}\pi^*$ excited state as shown by the present work as well as an earlier one (Tewari and Mishra 1984) is not shown by the rearrangement of electronic charges in the triplet $n\text{-}\pi^*$ excited state. Thus whereas the singlet $n\text{-}\pi^*$ excitation is delocalized on the whole benzaldehyde molecule, the triplet $n\text{-}\pi^*$ excitation is mainly localized on the CHO group. This seems to hint towards an explanation as to why this molecule shows more photochemical reactivity in the triplet $n\text{-}\pi^*$ excited state than in the singlet $n\text{-}\pi^*$ excited state.

The dipole moment of benzaldehyde is predicted, by the present work, to increase by about 3·9 Debye consequent to the singlet $n\text{-}\pi^*$ excitation whereas it is predicted to decrease by about 1·2 Debye following the triplet $n\text{-}\pi^*$ excitation. The result for the singlet $n\text{-}\pi^*$ excited state is in a qualitative agreement with the earlier theoretical work (Srivastava and Mishra 1980). This confirms again that the conclusion of van der Donckt and Vogels (1972) that the singlet $n\text{-}\pi^*$ excited state dipole moment of benzaldehyde is appreciably smaller than the ground state value was incorrect.

4. Conclusions

This study leads to the following important conclusions:

(i) Geometry of benzaldehyde is non-planar in the triplet $n\text{-}\pi^*$ excited state. It is either planar in the singlet $n\text{-}\pi^*$ excited state or the potential surface of this excited state is fairly flat.
(ii) A new feature is found regarding the molecular orbitals of benzaldehyde *i.e.*, some of them cross in going from the ground state to the triplet or singlet $n\text{-}\pi^*$ excited state.

(iii) The para-directing effect for electronic charges holds true in the singlet $n-\pi^*$ excited state but not in the triplet $n-\pi^*$ excited state. The triplet $n-\pi^*$ excitation of benzaldehyde is localized on the CHO group whereas the singlet $n-\pi^*$ excitation is delocalized over the whole molecule.

(iv) The $n-\pi^*$ singlet excited state dipole moment of benzaldehyde is appreciably larger than the ground state value whereas the reverse is true for the triplet excited state.

Acknowledgements

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