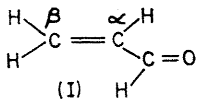
Shapes of Triplet States of Acraldehyde

By J. J. McCullough, Helen Ohorodnyk, and D. P. Santry*
(Chemistry Department, McMaster University, Hamilton, Ontario, Canada)

Enones ($\alpha\beta$-unsaturated ketones) undergo a variety of photochemical reactions.[1–3] Some of these, such as the *cis–trans*-isomerization of the acyclic[3] and seven- and eight-membered ring cyclic[2] derivatives, must be a result of geometrical changes in an excited state. Generally, enone photochemistry in solution proceeds *via* triplet states.[4] Although the geometries of the lowest triplet states—most likely to be photochemically active—are therefore of great interest, information concerning triplet geometry in the enone system is apparently lacking.



(I)

In view of the success of the CNDO method[5] in calculating excited-state geometries for molecules of known structure, it is reasonable to assume that a theoretical approach based on this method should give reliable excited-state structure for enones. We now report the results of such calculations for the geometries of the two lowest triplet states of acraldehyde (I), a model for the enone system. These calculations suggest that the equilibrium configuration of the $\pi^* \leftarrow n$ triplet state of acraldehyde should be planar, and that of $\pi^* \leftarrow \pi$ triplet should be nonplanar.

The geometry of acraldehyde, in its ground and two lowest triplet states, was investigated using CNDO (complete neglect of differential overlap) molecular orbital theory.[5] Specifically, the energies for these states were calculated as functions of three out-of-plane bending co-ordinates in order to determine whether any of the states is nonplanar. The bending co-ordinates investigated were the displacement of the oxygen out of the molecular plane, the rotation of the CHO group about the C–C bond and the rotation of the CH_2 group about the C^α–C^β bond. Changes in bond length were not considered in detail.

The calculations for the ground state of acraldehyde were based on the experimental bond lengths and in-plane bond angles reported by Brand and Williamson.[6] As the geometry of the triplet $\pi^* \leftarrow n$ state is unknown, the calculations for this state were based on the experimental data for the singlet $\pi^* \leftarrow n$ state.[6] The choice of bond lengths, *etc.*, for the $\pi^* \leftarrow \pi$ state calculation presented a more difficult problem, since the geometries of both singlet and triplet state are unknown. Duplicate calculations were therefore made for this state using the structural data for the ground state and the singlet $\pi^* \leftarrow n$ state, respectively. These two sets of calculations were found to be qualitatively very similar, but suggested that the C^α–C^β bond length for the $\pi^* \leftarrow \pi$ state is closer to the ground state value than to the $\pi^* \leftarrow n$ value. For this reason we report only the calculations for the triplet $\pi^* \leftarrow \pi$ state which are based on the ground-state bond lengths.

The calculations for the ground state of acraldehyde showed it to be planar with respect to all three out-of-plane bending co-ordinates.

The lowest triplet state of acraldehyde was found to be of $^3A''$ symmetry, and $\pi^* \leftarrow n$ in character. The calculations for this state were based on the Pople–Nesbet approximate open-shell theory.[7] According to these calculations the triplet $\pi^* \leftarrow n$ is planar with respect to all three out of plane bending co-ordinates.

The next highest triplet state was found to be $^3A'$ symmetry and $\pi^* \leftarrow \pi$ in character. The open-shell calculations for this state converged for the planar configuration of acraldehyde, but tended to diverge for the twisted configurations. For this reason the virtual orbital approximation was adopted for the investigation of the nonplanar configuration of this state. Although the virtual orbital method is not as satisfactory as the approximate open-shell treatment, it has been shown to yield reasonable excited-state geometries.[5] Furthermore, the few results which could be gleaned from the open-shell calculations for this state closely parallel the virtual orbital results. According to the calculations, the triplet $\pi^* \leftarrow \pi$ state of acraldehyde is planar with respect to the first two out-of-plane bending co-ordinates, but nonplanar with respect to the third (CH_2 twisting) co-ordinates. The equilibrium angle of rotation for the CH_2 group was calculated to be approximately 72°. It is difficult to calculate this angle accurately since it is fairly sensitive to the choice of the C^{α}–C^{β} bond length. In fact, the present calculations, based on the two sets of bond lengths, suggest that the rotation of the CH_2 group must be accompanied by significant changes in the C^{α}–C^{β} bond-length.

Finally, the potential curves, with respect to the rotation of the CH_2 group about C^{α}–C^{β}, for the ground state and triplet $\pi^* \leftarrow n$ and $\pi^* \leftarrow \pi$ states are shown in the Figure. The relative displacements of these curves are only qualitative since the energies have been minimized with respect to only three internal co-ordinates, and have been calculated at different levels of approximation. Nevertheless, they do provide a reasonable qualitative description of the lowest triplet states of acraldehyde. The small barrier to rotation of the CH_2 group in the triplet $\pi^* \leftarrow \pi$ state is particularly interesting.

These results concur with those of Zimmerman *et al*,[8] in predicting that the $\pi^* \leftarrow n$ triplet should have the lower energy in the planar configuration.

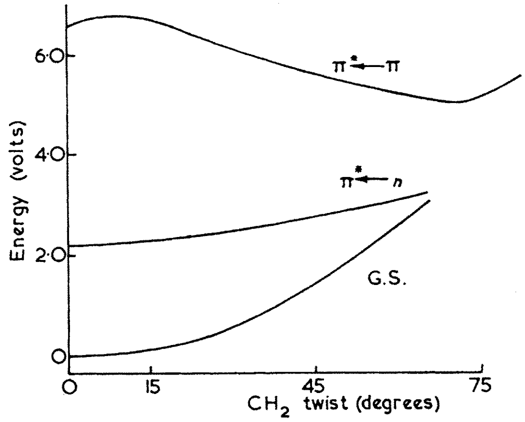


FIGURE. *Potential curves for the ground state, triplet* $\pi^* \leftarrow$ n *state, and triplet* $\pi^* \leftarrow \pi$ *state of acraldehyde. The displacements of these curves are only qualitative since each state was calculated at a different level of approximation.*

It is clear that the nonplanar character of the $\pi \leftarrow \pi^*$ triplet must be taken into account, whenever enone photochemistry in solution is being considered.

We thank the National Research Council of Canada for financial support.

(*Received, February* 20*th*, 1969; *Com.* 235.)

---

[1] For reviews, see K. Schnaffner, *Adv. Photochem.*, 1966, **4**, 81, on rearrangements, and P. E. Eaton, *Accounts Chem. Res.*, 1968, **1**, 50, for photo-additions.

[2] P. E. Eaton and K. Lin, *J. Amer. Chem. Soc.*, 1965, **87**, 2052; E. J. Corey, M. Tada, R. LeMahieu, and L. Libit, *ibid.*, p. 2051; P. E. Eaton and K. Lin, *ibid.*, 1964, **86**, 2087.

[3] R. A. Schneider and J. Meinwald, *J. Amer. Chem. Soc.*, 1967, **89**, 2023; M. J. Jorgenson and N. C. Yang, *ibid.*, 1963, **85**, 1969.

[4] H. E. Zimmerman, R. G. Lewis, J. J. McCullough, A. Padwa, S. W. Staley, and M. Semmelhack, *J. Amer. Chem. Soc.*, 1966, **88**, 1965; P. E. Eaton and W. S. Hurt, *ibid.*, p. 5038; J. L. Ruhlen and P. A. Leermakers, *ibid.*, 1967, **89**, 4944; E. Y. Y. Lam, D. Valentine, and G. S. Hammond, *ibid.*, p. 5712.

[5] J. A. Pople, D. P. Santry and G. A. Segal, *J. Chem. Phys.*, 1965, **43**, S129; J. A. Pople and G. A. Segal, *ibid.*, 1966, **44**, 3289; H. W. Kroto and D. P. Santry, *ibid.*, 1967, **47**, 792; H. W. Kroto and D. P. Santry, *ibid.*, p. 2736.

[6] J. C. D. Brand and D. G. Williamson, *Discuss. Faraday Soc.*, 1963, **35**, 184.

[7] J. A. Pople and R. K. Nesbet, *J. Chem. Phys.*, 1954, **6**, 571.

[8] H. E. Zimmerman, R. W. Binkley, J. J. McCullough, and G. A. Zimmerman, *J. Amer. Chem. Soc.*, 1967, **89**, 6589.