

Table 1. Symmetry coordinates for some planar five-membered ring structures.

| Species | Coordinate | (Models) |
|---------|--|------------------|
| A_1 | $2^{-1/2}(s_1+s_2)$ | (i, ii, iii, iv) |
| | $2^{-1/2}(d_1+d_2)$ | (i, ii, iii, iv) |
| | t | (i, ii, iii, iv) |
| | $(DT/2)^{1/2}(\beta_1+\beta_2)$ | (i, ii, iii, iv) |
| | $2^{-1/2}(q_1+q_2)$ | (ii, iv) |
| | $2^{-1/2}(r_1+r_2)$ | (iii, iv) |
| | $(QS/2)^{1/2}(\theta_1+\theta_2)$ | (ii, iv) |
| | $(RT/2)^{1/2}(\varphi_1+\varphi_2)$ | (iii, iv) |
| A_2 | $(ST/2)^{1/2}(\tau_1+\tau_2)$ | (i, ii, iii, iv) |
| | $[(DS)^{1/2}Q/2]^{1/2}(\gamma_1-\gamma_2)$ | (ii, iv) |
| | $[(DT)^{1/2}R/2]^{1/2}(\varepsilon_1-\varepsilon_2)$ | (iii, iv) |
| B_1 | $(ST/2)^{1/2}(\tau_1-\tau_2)$ | (i, ii, iii, iv) |
| | $[(DS)^{1/2}Q/2]^{1/2}(\gamma_1+\gamma_2)$ | (ii, iv) |
| | $[(DT)^{1/2}R/2]^{1/2}(\varepsilon_1+\varepsilon_2)$ | (iii, iv) |
| B_2 | $2^{-1/2}(s_1-s_2)$ | (i, ii, iii, iv) |
| | $2^{-1/2}(d_1-d_2)$ | (i, ii, iii, iv) |
| | $(DT/2)^{1/2}(\beta_1-\beta_2)$ | (i, ii, iii, iv) |
| | $2^{-1/2}(q_1-q_2)$ | (ii, iv) |
| | $2^{-1/2}(r_1-r_2)$ | (iii, iv) |
| | $(QS/2)^{1/2}(\theta_1-\theta_2)$ | (ii, iv) |
| | $(RT/2)^{1/2}(\varphi_1-\varphi_2)$ | (iii, iv) |

It is intended to use the present symmetry coordinates in a spectroscopic analysis of 1,3,4-thiadiazole to be performed in connection with a gas electron-diffraction investigation of this molecule.

1. Bak, B., Nygaard, L., Pedersen, E. J. and Rastrup-Andersen, J. *J. Mol. Spectry.* **19** (1966) 283.
2. Sbrana, G. and Ginanneshi, M. *Spectrochim. Acta* **22** (1966) 517.
3. Momany, F. A. and Bonham, R. A. *J. Am. Chem. Soc.* **86** (1964) 162.
4. Bak, B., Christensen, D., Hansen-Nygaard, L. and Rastrup-Andersen, J. *J. Mol. Spectry.* **7** (1961) 58.
5. Bak, B., Christensen, D., Dixon, W. B., Hansen-Nygaard, L., Rastrup-Andersen, J. and Schottländer, M. *J. Mol. Spectry.* **9** (1962) 124.

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The Influence of Methyl Groups on Electron Distribution and Photocycloaddition Reactions of α,β -Unsaturated Carbonyl Compounds

BJÖRN AKERMARK

Department of Organic Chemistry, Royal Institute of Technology, Stockholm 70, Sweden

Although the photocycloaddition of α,β -unsaturated carbonyl compounds to olefins and related reactions have been extensively studied in recent years,¹ some aspects of the mechanism remain obscure. One interesting problem is the nature of the attack of the excited carbonyl compound on the olefin.

The carbonyl compound, generally in the $n \rightarrow \pi^*$ excited state,¹ could behave either as an electrophile or as a diradical. When several isomeric addition products are possible, their relative yields should be determined, in an electrophilic type of reaction by the charge distribution but in a radical type of reaction by the unpaired electron density in the highest occupied

Table 1. Relative charge in the first $n \rightarrow \pi^*$ excited state of acrolein and its 2- and 3-methyl derivatives.

| | $h\nu$ | Charge on atom | | | |
|--|--------|----------------|----------------|----------------|----------------|
| | | O ^a | C ₁ | C ₂ | C ₃ |
| Acrolein | 1 | 0.54 | 0.25 | 0.16 | 0.05 |
| | 2.5 | 0.35 | 0.31 | 0.20 | 0.15 |
| 2-Methyl acrolein "inductive model" | 1 | 0.53 | 0.17 | 0.36 | -0.06 |
| | 2.5 | 0.34 | 0.23 | 0.38 | 0.05 |
| "hetero atom model" | 1 | 0.68 | 0.37 | 0.35 | 0.15 |
| | 2.5 | 0.50 | 0.43 | 0.38 | 0.26 |
| 3-Methylacrolein "inductive model" | 1 | 0.48 | 0.15 | 0.07 | 0.30 |
| | 2.5 | 0.33 | 0.18 | 0.10 | 0.38 |
| "hetero atom model" | 1 | 0.66 | 0.37 | 0.27 | 0.25 |
| | 2.5 | 0.49 | 0.40 | 0.31 | 0.34 |

^a Corrected with +1 corresponding to loss of the n -electron.

orbital of the excited carbonyl compound (*cf.*, however, below). It seemed interesting to calculate the substituent effects on these properties and to determine whether either of them could be correlated with available experimental data.

Using the Hückel molecular orbital (HMO) approximation, the charge distribution and unpaired π -electron density were calculated for the first $n \rightarrow \pi^*$ excited states of acrolein and its 2- and 3-methyl derivatives. The calculations (Table 1) indicate that in the $n \rightarrow \pi^*$ excited state of acrolein and 2-methyl acrolein the 2-position is more positive than the 3-position but in 3-methylacrolein this is reversed. The oxygen is of course very positive in all cases. By contrast, the unpaired electron density in the highest occupied orbital of the excited acroleins is always higher in the 3- than in the 2-position and low on the oxygen (Table 2). The radical type of

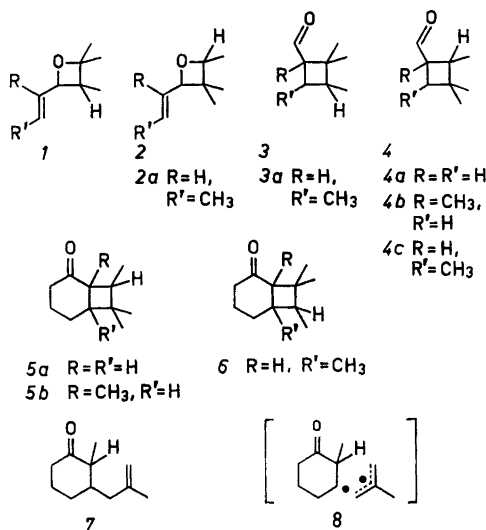


Table 2. Unpaired electron density in the first excited a orbital (c^2) of acrolein and its 2- and 3-methyl derivatives.

| | h_O | c^2 on atom | | | |
|--|-------|---------------|----------------|----------------|----------------|
| | | O | C ₁ | C ₂ | C ₃ |
| Acrolein | 1 | 0.18 | 0.33 | 0.05 | 0.43 |
| | 2.5 | 0.06 | 0.44 | 0.02 | 0.48 |
| 2-Methyl acrolein "inductive model" | 1 | 0.21 | 0.39 | 0.04 | 0.35 |
| | 2.5 | 0.07 | 0.48 | 0.02 | 0.43 |
| "hetero atom model" | 1 | 0.19 | 0.36 | 0.05 | 0.40 |
| | 2.5 | 0.06 | 0.46 | 0.02 | 0.46 |
| 3-Methyl acrolein "inductive model" | 1 | 0.15 | 0.40 | 0.03 | 0.42 |
| | 2.5 | 0.06 | 0.49 | 0.00 | 0.45 |
| "hetero atom model" | 1 | 0.17 | 0.34 | 0.02 | 0.43 |
| | 2.5 | 0.06 | 0.44 | 0.00 | 0.46 |

addition of all the excited acroleins to, *e.g.*, isobutylene would be expected to give mainly a mixture of the cyclobutanes 3 and the oxetanes 2. By contrast, mainly the cyclobutanes of type 4, but 3-methylacrolein of type 3.

In the acrolein series only the addition of 3-methylacrolein to isobutylene has

been reported.³ The cyclobutane 4c and the oxetane 2a appear to be the main products. 4c is the "wrong" adduct for both types of addition, but if it is assumed that the influence of the methyl group is less than calculated, 4c could be formed in an electrophilic type of addition.

In the cyclohexenone series, the photoaddition of cyclohexenone and 3-methylcyclohexenone to isobutylene gave the cyclobutanes 5a and 6 in accordance with the predictions for an electrophilic reaction (Table 1). 2-Methylcyclohexenone according to our predictions should give 5b since the 2-position should be even more positive than in cyclohexenone. Instead a complex mixture of products³ was obtained, the major of which was probably 7.⁴ This may indicate that a radical addition is preferred for steric reasons. There is also the possibility that the hydrogen abstraction has electrophilic character in spite of the fact that a hydrogen atom is transferred. The product 7 would then be formed via the intermediate diradical pair 8 (*cf.* azoester and cyclohexene).⁵

Of the reported photoreactions of α,β -unsaturated carbonyl compounds only the enone rearrangement clearly has radical character.⁶ The products are in accordance with the radical model described here. However, in photoadditions as in "normal" radical reactions, the stability of the intermediate radicals or diradicals,⁷ rather than the unpaired electron density may

determine the product composition. In the enone case both radical models predict the same products, but the high stereospecificity of the reaction⁶ seems to imply that bond formation and thus the free radical density is the most important factor.

It seems clear that the photo cyclo addition of α,β -unsaturated carbonyl compounds to olefins has partial electrophilic character. However, the approximative nature of the present calculations and the lack of experimental data make the conclusions uncertain. More refined calculations and more experiments are under way in an attempt to clarify the situation.

Experimental. The parameters used in the Hückel MO calculations were essentially those recommended by Streitwieser:⁸ $\alpha_{=O} = \alpha + \beta$, $\beta_{C=O} = \beta$, $\alpha_{C-CH_3} = \alpha - 0.5\beta$ ("inductive model"), $\alpha_{CH_3} = \alpha + 2\beta$, $\beta_{C-CH_3} = 0.7\beta$ ("hetero atom model"). It was assumed that the oxygen n -electron could be incorporated in the π^* -orbital without corrections. However, since the electron affinity of the carbonyl oxygen should be considerably higher in the $n \rightarrow \pi^*$ excited state than in the ground state, calculations were also carried out using $\alpha_{=O} = \alpha + 2.5\beta$. The results of the calculations are presented as electron density in the first excited orbital (Table 2) and relative charge (Table 1). The charge on the oxygen is corrected for the loss of one n -electron.

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1. For reviews, see e.g. Kan, R. O. *Organic Photochemistry*, McGraw, New York 1966, pp. 185, 198; Neckers, D. C. *Mechanistic Organic Photochemistry*, Reinhold, New York 1967, pp. 131, 138; Chapman, O. L. and Lenz, G. In Chapman, O. L. *Organic Photochemistry*, Dekker, New York 1967, Vol. 1, p. 283.
2. Yang, N. C. *Pure Appl. Chem.* **9** (1964) 591.
3. Corey, E. J., Bass, J. D., LeMahieu, R. and Mitra, R. B. *J. Am. Chem. Soc.* **86** (1964) 5570.
4. Schneider, R. A. and Meinwald, J. J. *Am. Chem. Soc.* **89** (1967) 2023.
5. Ahlgren, G., Åkermark, B. and Dahlquist, K. *Acta Chem. Scand.* **22** (1968) 1129.

6. Zimmerman, H. E., Rieke, R. D. and Scheffer, J. R. *J. Am. Chem. Soc.* **89** (1967) 2033.

7. Bartlett, P. D. *Science* **169** (1968) 833.

8. Streitwieser, A. *Molecular Orbital Theory for Organic Chemists*, Wiley, New York 1961, p. 135.

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Adaptation of the 2,4-Dinitrophenylhydrazine Method for Determination of Ascorbic Acid after Separation by Column Chromatography

ULF FRIBERG, STEFAN LOHMÄNDER
and GUNILLA CARLSSON

Department of Histology, Karolinska Institutet, Fack, S-104 01 Stockholm 60, Sweden

The colorimetric procedure, based on the reagent 2,4-dinitrophenylhydrazine (2,4-DNPH), developed by Roe *et al.*,¹⁻⁴ is the most specific and most commonly used method for the determination of ascorbic acid (AA) in biological materials. In this procedure, a trichloroacetic acid (blood, urine) or metaphosphoric acid (plant materials) filtrate is shaken with active charcoal and filtered. The charcoal clarifies the solution and oxidizes the AA to dehydroascorbic acid (DHA). The filtrate is incubated with 2,4-DNPH for 3 h at 37°C in the presence of thiourea. Sulfuric acid, 16 M, is then added to the tubes in an ice bath. After 30 min absorption is measured at 520 nm in a colorimeter.

In its original version, the method is rather laborious and time-consuming. The present paper describes a simplified version which permits the convenient processing of a large number of samples. It was developed for use with a column chromatographic procedure for the assay of trace amounts of vitamin C in dried feed stuffs.⁵ The adaptation of the 2,4-DNPH method for large scale work involves the use of 2,6-dichlorophenolindophenol (2,6-DCPI) as oxidant. Incubation is carried out at an elevated temperature for 1 h. Full use is