

THEORETICAL STUDY OF THE CONFORMATIONAL ARRANGEMENT OF 3-BENZYLIDENE-2,4-PENTANEDIONE AND ITS SUBSTRUCTURES

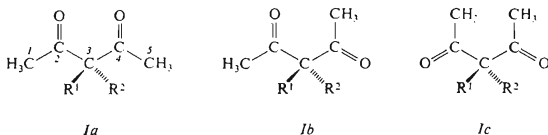
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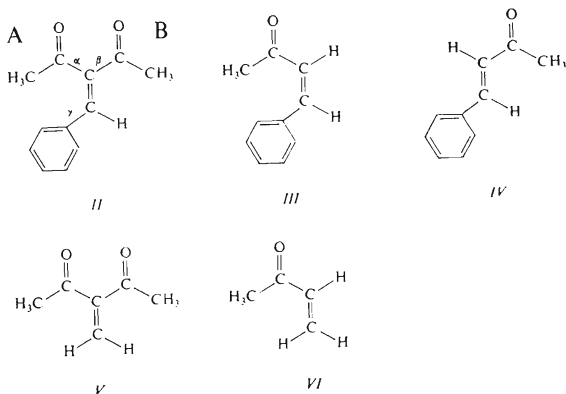
The quantum chemical PCILO method was employed for calculation of conformational maps of 3-benzylidene-2,4-pentanedione. The analogous conformational maps of simpler substructures were also investigated to enable investigating the respective interactions. Steric interactions of the acetyl group with the phenyl group and of both acetyl groups were found to play a dominant role. One acetyl group is turned by 60° from the *s-cis* position, the other is in an *s-trans* conformation when being in the energetically more favourable sterical arrangement. The obtained data were compared with the experimental results.

The bonding conditions at the carbon between carbonyl groups are an important factor of conformational arrangement of acyclic carbonyl compounds. 3,3-Di-substituted derivatives of 2,4-pentanedione can exist in three plane arrangements (Scheme 1). Providing $R^1 = H$, the molecule is stabilized through formation of an intramolecular hydrogen bonding and the position of oxygens corresponds to conformation *Ia*. If there is no possibility to form a hydrogen bonding, steric and electrostatic interactions will be manifested. Experimental¹ and theoretical² investigations of 3,3-dimethyl-2,4-pentanedione showed that the most favourable conformation of the mentioned plane arrangement is *Ib*; further decrease of energy leads to deviation of one acetyl group off the plane. Were the carbon $C_{(3)}$ sp^2 hybridized, then a conjugated system is formed, this being a further factor influencing the molecule conformation. As a consequence, stabilization of the hydrogen bond is eliminated, the conjugation tacks the planarity of the system, unless steric conditions are involved. Here also three planar conformations are possible (Scheme 1).



SCHEME 1

As a continuation of the recent study on 3-benzylidene-2,4-pentanedione^{3,4}, this paper deals with the theoretical examination of its conformation, as well as with conformations of substructures derived of it (Scheme 2); the results obtained were confronted with the known experimental data.



SCHEME 2

CALCULATIONS

The quantum chemical PCIL0⁵⁻⁸ method was employed for this study; the dependence of the total energy upon rotational angles α , β and γ (Scheme 2) was investigated, the angles being rotated by 30°. The conformational arrangement of 3-benzylidene-2,4-pentanedione (II) is determined by several interactions modelled by simpler substructures III–VI. The formulas shown correspond to rotational angle values $\alpha = \beta = \gamma = 0^\circ$. The letter A in compound II refers to the acetyl group closer to the benzene ring, letter B stands for the second acetyl. Following geometric data⁹ were employed for calculations: $R_{C-C(\text{benzene})} = 0.1395$ nm, $R_{C-C} = 0.153$ nm, $R_{C=C} = 0.133$ nm, $R_{C=O} = 0.123$ nm, $R_{C-H} = 0.108$ nm, $R_{C-H(\text{methyl})} = 0.109$; all angles at $C_{sp^2} = 120^\circ$, those at $C_{sp^3} = 109.48^\circ$. Relationship between the energy and rotation of methyl groups of some substructures was determined; as shown, this factor is of no importance for the total energy change.

RESULTS AND DISCUSSION

3-Buten-2-one (VI) represents the simplest investigated substructure. The presence of a conjugated system of double bonds prefers a plane arrangement. The *s-trans* conformation of the structurally related acrolein¹⁰ was experimentally proved to be by 8 kJ mol⁻¹ more stable than the *s-cis* one. The planar *s-trans* arrangement is

mostly favoured also for compound *VI*. The difference between the *s-trans* and *s-cis* conformations was found to be 5 kJ mol^{-1} ; the lower value for acrolein than the experimental data can be rationalized by a steric interaction of the CH_3 group.

2-Methylene-2,4-pentanedione (*V*) contains two acetyl groups between which steric and coulombic interactions are engaged. The conjugation is weakened to some extent by a cross-conjugation. We calculated the dependence of the total energy upon the α and β angle values. Even here, planar arrangement of the molecule is mostly favourable. Fig. 1 shows the sector of the energy hypersurface; as it follows, one fragment $\text{HC}=\text{C}-\text{C}=\text{O}$ remains in the *s-trans* arrangement, whereas the second $\text{C}=\text{O}$ bond is in an *s-cis* conformation with respect to $\text{C}=\text{C}$ bond. Conformation *trans-s-trans* is less favourable ($\Delta E = 16\text{ kJ mol}^{-1}$) due to a repulsion of both oxygens; the least favourable is the *cis-s-cis* conformer with a great steric interaction of both methyl groups.

(*E*)-4-Phenyl-3-buten-2-one (*IV*) represents a conjugated system having the steric interactions quite restricted and therefore, the steric arrangement should be close to the planar one. The experimental investigation of conformation based upon IR spectra¹¹ and dipole moments¹² revealed that 3-phenyl-2-propenal occurs almost exclusively as an *s-trans* conformer. Some steric interaction between CH_3 and *H* at the β -carbon was encountered with compound *IV*; it represents an equilibrium

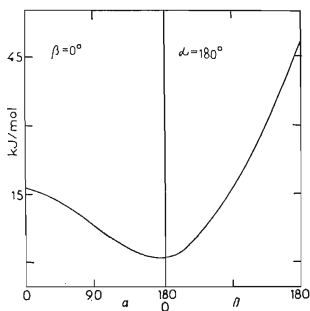


FIG. 1

Relationship between the total energy of 2-methylene-2,4-pentanedione (*V*) and rotation of the acetyl groups

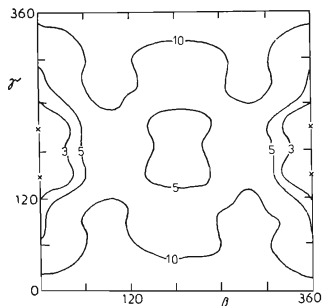


FIG. 2

Relationship between the total energy of (*E*)-4-phenyl-3-buten-2-one (*IV*) and rotational angles β and γ

mixture of *s-trans* and *s-cis* in a 57 : 43 ratio. This phenomenon can be generalized to compounds containing the fragment —HC=CH—CR=O : the increase of the bulkiness of substituent R attached to the carbonyl carbon causes a decrease of the *s-trans*/*s-cis* ratio. The relationship between the energy of (*E*)-4-phenyl-3-buten-2-one (*IV*) and rotational angles β and γ is seen in Fig. 2; in line with the experiment, more favourable is the *s-trans* conformation. The absolute energy minimum does not fully correspond to the planar arrangement, the benzene ring is a little bit rotated with respect to the C=C—C=O fragment. This nonplanarity is, however, negligible, since the energy difference between the planar and the out-of-plane form is only 1 kJ mol^{-1} . A similar nonplanarity can be encountered e.g. with styrene¹³; it might be associated with the character of the PCILO method. The second minimum is associated with the *s-cis* conformation. The calculated energy difference between the *s-cis* and *s-trans* conformers of compound *IV* is 3.8 kJ mol^{-1} .

Steric interactions of the acetyl group with benzene ring are evidently pronounced with (*Z*)-4-phenyl-3-buten-2-one (*III*). Fig. 3 shows the conformational map of the dependence between the total energy and rotational angles α and γ . The region of the great steric repulsion is shaded; as seen, the energy minima correspond to the rotation of the acetyl group by 60° from the *s-cis* and also from the *s-trans* positions. The benzene ring is turned from the plane by 30° . Transitions among the separate minima require considerably more energy when compared with the afore-mentioned compound. A noticeable disturbance of conjugation takes place due to great steric interactions.

All types of interactions mentioned so far become manifested in 3-benzylidene-2,4-pentanedione (*II*). As evidenced by spectral measurements¹⁴, the acetyl B is coplanar and *s-trans* oriented with respect to C=C , whereas the acetyl A is turned by approxi-

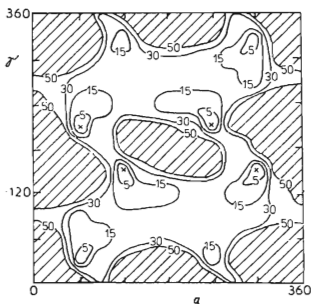


FIG. 3

Relationship between the total energy of (*Z*)-4-phenyl-3-buten-2-one (*III*) and rotational angles α and γ

mately 45° from the *s-cis*-planar position. Based upon IR data³, the more favourable was such a conformation, where the acetyl A has an arrangement close to *s-cis*, but is, nevertheless, turned of the plane and the acetyl B is *s-trans*, coplanar with C=C. Similar results afforded the ¹³C NMR spectra⁴. The IR investigations^{3,14} suppose an existence of an equilibrium mixture of several conformations.

The most significant interactions of single steric and electronic effects are those in substructure V, and especially the steric interactions in substructure III. Therefore, the conformation map, showing the dependence of total energy of compound II upon rotational angles α and γ (Fig. 4), can be considered as a superposition of analogous dependences for compounds III and V. The absolute energy minimum in Fig. 4 represents the rotation of acetyl group A by 60° of the *s-cis* plane arrangement. Similarly as in structures III and IV, also in II the phenyl group is turned by 30° with respect to C=C. Fig. 4 displays the dependence at constant value of the rotational angle $\beta = 0^\circ$. The effect of the angle β change upon the total energy was investigated, too. As seen, substructures II and IV tend to have the acetyl groups B in an *s-trans* arrangement. Due to the rotation of the acetyl A in compound II by 60° a steric interaction with the acetyl B takes place and consequently, it will not be perfectly coplanar with C=C, but turned by 30° . The energy change associated with this is very small (0.4 kJ mol^{-1}). Fig. 5 shows calculation of the optimum structure of compound II with rotational angles $\alpha = 120^\circ$, $\beta = 30^\circ$, $\gamma = 150^\circ$. This calculation is in a relatively good accordance with the above-mentioned experimental data. The

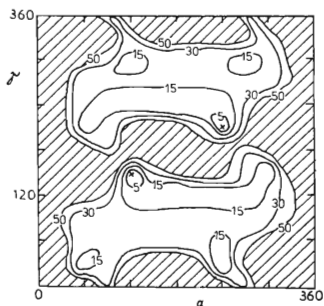


FIG. 4

Relationship between the total energy of 3-benzylidene-2,4-pentanedione (II) and rotational angles α and γ .

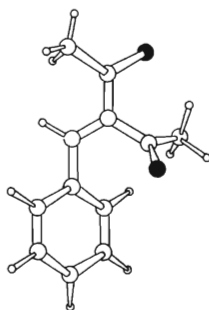


FIG. 5

Optimal structure of 3-benzylidene-2,4-pentanedione ($\alpha = 120^\circ$, $\beta = 30^\circ$, $\gamma = 150^\circ$).

results also evidence the possibility of existence of several conformations in the equilibrium mixture. Further local minimum is seen in Fig. 4; its higher energy by 11 kJ mol⁻¹ corresponds to rotation of the acetyl A by 60° from *s-trans* position.

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