

CONFORMATIONS OF MOLECULES BEARING TWO CARBONYL GROUPS ON ADJACENT ATOMS

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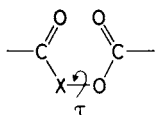
Dedicated to the memory of Dr K. Bláha.

Conformation of α -acyloxyketones *IIIa*–*IIIc* was determined from their dipole moments in benzene solution. Around the C—O bond the *ap* conformation prevails over *sc*, around the C—C bond several conformations are present and those with a larger distance between the two carbonyl oxygens are preferred. The conformation is thus quite different than in crystal. Similarities of the crystal conformations of *III* to *I* or *II* are due mainly to crystal packing forces, while the interaction of the two carbonyl oxygen atoms is of little importance.

Conformations of diacyl peroxides (*I*) and N,O-diacylhydroxylamines (*II*) are very similar in crystal^{1,2} as well as in solution^{3–5}. The two planar moieties of the molecule intersect in the X—O bond and are almost perpendicular to each other, the most probable values of the dihedral angle being between 70 and 90°. The steric arrangement of diacyl disulphides⁶, diacyl diselenides⁷, diacyl ditellurides⁸ and diacylhydrazines⁹ is essentially the same. Theoretical explanation of the nonplanar conformation of the four inner atoms was sought always in the repulsion of the lone electron pairs¹, although there has been no agreement about their steric orientation and hybridization. The problem may be traced back to hydrogen peroxide but correct theoretical calculations are extremely difficult¹ even for this simplest model compound.

Almost identical conformations of so different compounds suggest the question of whether they are actually controlled only by electron repulsion at the central bond, or whether even interactions of the remote carbonyl groups are of some importance. For this reason we took interest¹⁰ in compounds *III* where one of the central atoms is an sp^3 carbon. This substitution changes the character of the molecule profoundly. Firstly, the conformation of the left hand moiety in *III* need be no longer planar, i.e. the dihedral angle Θ in *IIIa* may differ from zero and a rather low rotational barrier

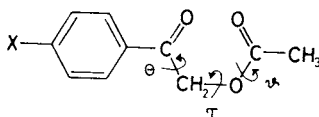
is anticipated. Secondly, the potential energy of rotation around the C—O bond (dihedral angle τ in *IIIa*) should be also different, an equilibrium of the *sc* and *ap* rotamers being expected (τ near to 60° and 180° , respectively). In the Cambridge Structural Database¹¹ (CSD) we retrieved X-ray structures of 21 compounds containing 24 fragments *III*. It was rather surprising to find that the conformations are again very similar to those of *I* or *II*, the values of τ were between 60° and 106° , Θ



I, X = O

II, X = NH

III, X = CH₂



IIIa, X = H

IIIb, X = Br

IIIc, X = NO₂

mostly lower than 10° . One could argue that most of the structures retrieved were rather complex, with considerable steric hindrance (e.g. many steroid derivatives), some other determinations could be less accurate due to presence of heavy atoms. Therefore, we undertook an X-ray study of 2-acetoxy-1-(4-nitrophenyl)ethanone¹⁰ (*IIIc*) which represents a simple model compound with a sufficiently high melting point. The result was again the same: $\tau = 79^\circ$, $\Theta = 2^\circ$. In this note we report on the conformation in solution as determined from dipole moments of *IIIa*–*IIIc*. The results are compared with the X-ray structures^{10,11} of *III* on the one hand and with the conformation of *I* and *II* on the other.

EXPERIMENTAL AND RESULTS

Materials. 2-Acetoxy-1-phenylethanone¹² (*IIIa*), m.p. 48°C (ether); 2-acetoxy-1-(4-bromophenyl)ethanone¹³, (*IIIb*), m.p. 85°C (ethanol-water). 2-Acetoxy-1-(4-nitrophenyl)ethanone (*IIIc*), m.p. 122°C (ethanol), was prepared according to literature¹⁴, identity with the material previously described¹⁵ as 2-hydroxy-1-(4-nitrophenyl)ethanone was confirmed.

Measurements of dipole moments. The measurements according to the method of Halverstadt and Kumler¹⁶ were carried out in benzene solution at 25°C . As a rule five solutions of different concentration were prepared within the range of weight fractions $w_2 = 0.0008$ – 0.006 . Relative permittivities of the solutions, ϵ_{12} , were measured on a heterodyne apparatus at the frequency of 1.2 MHz; the measuring cell was calibrated with specially purified benzene, $\epsilon = 2.27379$. Densities were measured with an Ostwald-Sprengel pycnometer. Benzene used for routine measurements had the physical constants: $\epsilon_1 = 2.2763$, $d_4^{-1} = 1.14486$.

The molar refractions were calculated by summing Vogel's atom increments¹⁷ valid at 20°C . For the substituents on the benzene ring increments were used as derived directly from benzene mono derivatives, while the conjugation $\text{C}_6\text{H}_5\text{—CO}$ was accounted for by an additional correction term of 0.85 cm^3 . The atomic polarization (P_A) was taken into account by a correction

TABLE I

Polarization data and dipole moments of substituted 2-acetoxy-1-phenylethanones *IIIa-c* (benzene, 25°C)

Parameter	<i>IIIa</i>	<i>IIIb</i>	<i>IIIc</i>
α^a	5.33	2.79	6.38
β^a	-0.305	-0.465	-0.420
P_2^0 , cm ³ mol ⁻¹	223.0	186.8	315.6
R_D , cm ³ mol ⁻¹	47.3	55.1	53.7
$\mu \cdot 10^{30}$, C m ^b	9.7	8.4	11.9
μ_{calc} (free rotation) ^c	11.8	10.4	12.9
μ_{calc} ($\tau = 60^\circ$) ^d	12.6	12.0	15.2
μ_{calc} ($\tau = 180^\circ$) ^d	9.9	6.9	9.1

^a Slopes of the plots ϵ_{12} and d_{12}^{-1} , respectively, versus the weight fraction w_2 ; ^b correction for the atomic polarization 5% of the R_D value; ^c anticipated free rotation around both the C—O and C—C bonds; ^d free rotation around the C—C bond assumed.

of 5% of the R_D value¹⁸. The results are listed in Table I. The reproducibility of dipole moments may be estimated to 0.2, but values lower than 5 are loaded with greater errors due to the correction for P_A (all dipole moment values in 10^{-30} C m).

Calculations. The theoretical dipole moments were calculated by vector addition of standard bond moments¹⁹: H—C_{ar} 1, H—C_{ar} 0, C—O 2.47, C=O 8.33, C_{ar}—Br 5.23, and the group moment C_{ar}—NO₂ 13.33. Conjugation C₆H₅—CO was expressed by a vector term of 1.67 in the direction C_{ar}—C, this correction was derived²⁰ from the experimental value of acetophenone. The bond angles were taken from the X-ray structure¹⁰ of *IIIc*.

Dipole moments for the free rotation were calculated according to the formula

$$\mu_{\text{eff}}^2 = \mu_1^2 + \mu_2^2 + \mu_3^2 + 2\mu_1\mu_2 \cos \varphi_1 \cos \varphi_2 \cos \omega_{12} + 2\mu_1\mu_3 \cos \varphi_1 \cos \varphi_3 \cos \omega_{13} + 2\mu_2\mu_3 \cos \varphi_2 \cos \varphi_3 \cos \omega_{23}$$

when three dipoles $\mu_1 - \mu_3$ rotate around the axes $q_1 - q_3$, respectively, φ are the angles of a dipole with the respective axis, and ω are angles between axes.

The CSD search was carried out with the May 1987 version¹¹ containing 56 642 entries. Retrieved were compounds with the fragment O=C—O—CH₂—C=O, not forming part of a heterocycle. Compounds with heavy metals, disordered structures and those with the *R* factor >0.1 were discarded. Compounds investigated several times were included only once. Several functions in one molecule or several molecules in the cell were taken separately. Compounds with Br or I were considered as a particular subgroup (17 items), but after a preliminary examination they were combined with the others (together 29 items).

DISCUSSION

The molecule of *III* has two degrees of freedom, viz. the dihedral angles τ and Θ . Their values are zero in the conformation pictured in the formula *III*, positive values

of both angles represent rotation of the two carbonyl oxygens to opposite sides of the OCC plane. However, all possible angles are not physically acceptable, particularly τ can acquire only values near to 60° , 180° , and 240° , corresponding to staggered conformations. The experimental dipole moments can be in principle interpreted in two ways: *a*) by a single conformation, *b*) by an equilibrium of two or more conformations. In the former case the values of τ and Θ are obtained directly from experiment, but they need not be physically possible. In the latter case an infinite number of solutions is possible; if one assumes some probable conformations, one obtains from the experiment their population.

We calculated the dipole moments for all combinations of τ and Θ , and plotted their squared values in graphs²¹ comparing always two compounds. A network of curves was obtained, each corresponding to one fixed and one variable dihedral angle. Only a few of these curves are shown in Figs 1 and 2; they are either ellipses or reduced to straight lines, some ellipses are unrecognizable in the scale of the graphs. Figs 1 and 2 reveal first that the conformation in solution is different from that in crystal (point 4), and no simple conformation with $\Theta = 0$ is possible. If one wanted to interpret the dipole moments by a single conformation, there would be two solutions: either $\tau = 125^\circ$ and $\Theta = -35^\circ$, or $\tau = 110^\circ$ and $\Theta = 130^\circ$. Both are unacceptable since the conformation around the C—O bond would be almost exactly eclipsed. Therefore, we are obliged to consider the presence of several rotamers in equilibrium. The hypothesis of statistical population of all possible conformations (the so-called free rotation²²) can be rejected (point 1 in Figs 1 and 2). Another plausible hypothesis would be an equilibrium of staggered conformations around the C—O bond (τ either 60° or 180°) combined with a practically free rotation around C—C. This possibility is pictured in Figs 1 and 2 by the points 2 and 3, any mixture of the two forms would be in our graphical representation²¹ situated on the connecting line of these two points, the distances being proportional to the populations. The figures reveal that the statistical population $ap : sc = 1 : 2$ does not match with the experiment, on the contrary the ap conformation is more populated, in a ratio approximately 2 : 1. In addition, the experimental point would be somewhat shifted from the possible connecting line showing that the rotation around the C—C bond is not completely free, but the forms with lower dipole moments (i.e. with a longer distance between the two carbonyl oxygens) are somewhat preferred. We have still to consider that the angle τ in the sc form need not be exactly 60° but is probably slightly widened. If it were equal to 79° (the crystallographic value), the above conclusions would keep their validity, only the ratio of the $ap : sc$ form would change to 3 : 2. To summarize only what has been proven with some reliability, we may state that there are two conformations around the C—O bond, ap and sc , the former prevailing, the latter with a possibly widened dihedral angle. Conformations around the C—C bond are numerous, not well defined, but those with a longer O...O distance are slightly preferred.

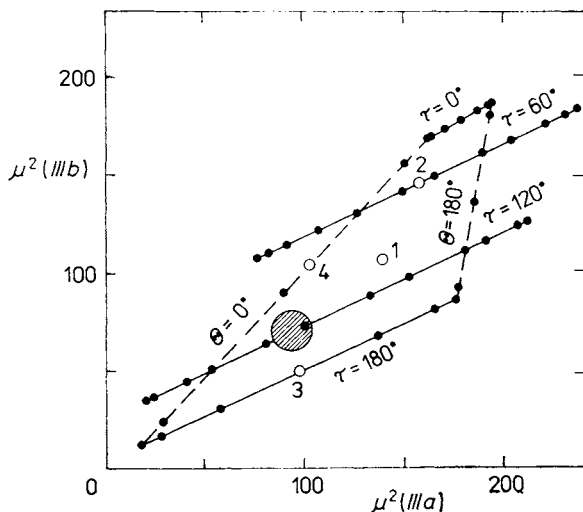


FIG. 1

Determination of the conformation of *III* by plotting the squared dipole moments of *IIIa* (x axis) and *IIIb* (y axis). The curves represent one fixed and one variable dihedral angle, the small points follow at the distances of 30° . Open points: 1 completely free rotation, 2 $\tau = 60^\circ$, free rotation around C—C, 3 $\tau = 180^\circ$, free rotation around C—C, 4 conformation in crystal. The experimental point is dashed

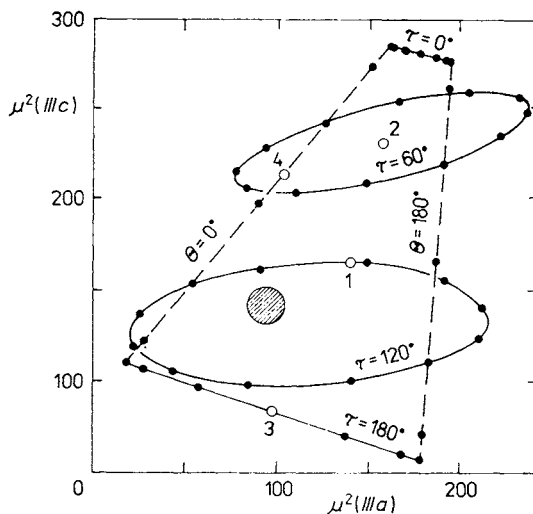


FIG. 2

Determination of the conformation of *III* by plotting the squared dipole moments of *IIIa* (x axis) and *IIIc* (y axis). See Fig. 1 for descriptive details

For a comparison with the solid state conformation we may refer either to our results¹⁰ on *IIIc*, or to mean values from 29 compounds retrieved from the CSD (ref.¹¹). The two sets agree extremely well (Table II), proving that the compound *IIIc* was well chosen as a simple and typical example. One salient feature of these data is the planar arrangement of the hydroxyketone fragment (the left hand moiety

TABLE II

Comparison of geometrical parameters of compounds *I–III* in the crystalline phase

Parameter	<i>IIIc</i> ^a	<i>III</i> ^b	<i>I</i> ^c	<i>II</i> ^d
τ	79	79	81–91	79–88
θ	2	7	—	—
ϑ	6	4	3–6	—
C—C—O	110.9	111	—	(116–117) ^e
C—O—C	115.9	116	107–111	(111–114) ^f
$r(\text{O}\cdots\text{O})$, pm	321	320	300–324	313–338

^a Ref.¹⁰; ^b median value of 29 compounds of the structure *III*, retrieved from CSD, ref.¹¹; ^c ref.¹ and references quoted therein; ^d ref.²; ^e the angle C—N—O; ^f the angle C—O—N.

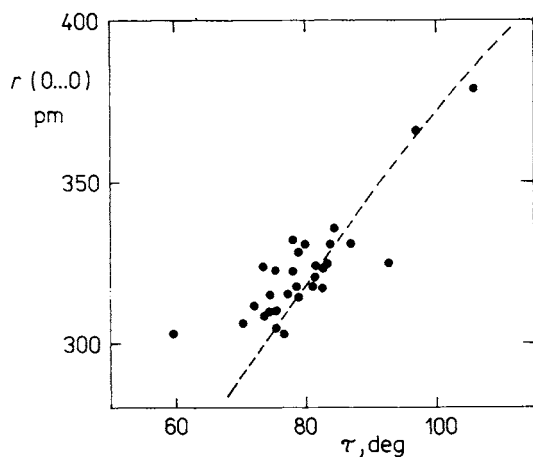


FIG. 3

Scatter plot of the non-bonded distance O \cdots O against the dihedral angle τ for 30 structures in the crystalline phase. The broken line represents the purely geometrical effect of rotating the two moieties of *III* around the C—O bond

in *III*): the dihedral angles θ are actually not larger than ϑ , which expresses the non-planarity of the ester group (the right hand moiety). While the latter is known to be planar both in crystal²³ and in free molecules²⁴, the planarity of the hydroxy-ketone fragment, not found in solution, should be due to crystal packing effects. Hence the puzzling agreement of crystal structures of *III* with *I* and *II* is partly fortuitous since the coplanarity of the left hand parts has different grounds. Let us now search for possible proofs of repulsive or even attracting forces between the two carbonyl groups. Concerning the bond angles C—CH₂—O and C—O—C, their mean values are quite normal (Table II). Although they are rather variable in individual compounds, any dependence on τ or on the O...O distance was not detected. More telling is a plot of the two latter quantities against each other (Fig. 3). The broken line represents purely geometrical relationship when the two planar moieties of *III* rotate around the C—O bond. It is approximately followed by many experimental points. If there is any interaction between the two carbonyls, the rotation around the C—C bond can bring the two O atoms into a more favourable distance. The experimental points would then deviate from the broken line either upwards if the O...O distance should be too narrow, or downwards if it should be too large. Fig. 3 gives evidence of the former effect: two or more points on the left are displaced upwards. Evidently the O...O distance cannot be reduced below some 300 pm which is practically the sum of the van der Waals radii. An opposite, attracting effect can hardly be proven. There are some deviations downwards in the right part of Fig. 3, but some points also follow the broken line up to $r(\text{O}\dots\text{O})$ of 380 pm. The deviations may be again due to crystal forces rather than to an actual attraction.

In conclusion, the conformations of *I*, *II* and of other compounds with lone pairs on the central bond⁶⁻⁹ are controlled essentially by repulsion of these electrons, the non-bonded interaction of the carbonyl oxygens being of minute importance. The similar conformation of *III* is due mainly to crystal packing forces and partly fortuitous. In solution, the conformation is fundamentally different and much more flexible; then the interaction between the two oxygens gets some importance.

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REFERENCES

1. Exner O. in the book: *The Chemistry of Peroxides* (S. Patai, Ed.), p. 85. Wiley, Chichester 1983.
2. Göttlicher S., Ochsenreiter P.: *Chem. Ber.* 107, 398 (1974).
3. Jehlička V., Plesničar B., Exner O.: *Collect. Czech. Chem. Commun.* 40, 3004 (1975).
4. Exner O.: *Collect. Czech. Chem. Commun.* 30, 652 (1965).
5. Artemenko A. I., Tikunova I. V., Anufriev E. K., Jehlička V., Exner O.: *Collect. Czech. Chem. Commun.* 46, 729 (1981).
6. Vasileva V. N., Guryanova E. N.: *Zh. Fiz. Khim.* 33, 1976 (1959).

7. Šindelář K., Exner O.: *Collect. Czech. Chem. Commun.* **37**, 2734 (1972).
8. Jehlička V., Piette J. L., Exner O.: *Collect. Czech. Chem. Commun.* **39**, 1577 (1974).
9. Lumbroso H., Barassin J.: *Bull. Soc. Chim. Fr.* **1964**, 3190.
10. Tinant B., Declercq J. P., Exner O.: *Bull. Soc. Chim. Belg.* **96**, 511 (1987).
11. Allen F. H., Bellard S., Brice M. D., Cartwright B. A., Doubleday A., Higgs H., Hummelink T., Hummelink-Peters B. G., Kennard O., Motherwell W. D. S., Rodgers R. J., Watson D. G.: *Acta Crystallogr.*, **B 35**, 2331 (1979).
12. Rather J. B., Reid E. E.: *J. Am. Chem. Soc.* **43**, 629 (1921).
13. Judefind W. L., Reid E. E.: *J. Am. Chem. Soc.* **42**, 1043 (1920).
14. Yagupolskii L. M., Butlerovskii M. A., Belinskaya R. V., Ivanova V. I.: *Zh. Obshch. Khim.* **30**, 1288 (1960).
15. Engler C., Zielke O.: *Ber. Dtsch. Chem. Ges.* **22**, 203 (1889).
16. Halverstadt I. F., Kumler W. D.: *J. Am. Chem. Soc.* **64**, 2988 (1942).
17. Vogel A. I.: *J. Chem. Soc.* **1948**, 1842.
18. Exner O.: *Collect. Czech. Chem. Commun.* **46**, 1002 (1981).
19. Exner O.: *Dipole Moments in Organic Chemistry*, p. 33. Thieme, Stuttgart 1975.
20. Plesničar B., Smolíková J., Jehlička V., Exner O.: *Collect. Czech. Chem. Commun.* **43**, 2754 (1978).
21. Exner O., Jehlička V.: *Collect. Czech. Chem. Commun.* **30**, 639 (1965).
22. Ref.¹⁹, p. 50–52.
23. Schweizer W. B., Dunitz J. D.: *Helv. Chim. Acta* **65**, 1547 (1982).
24. Exner O. in the book: *The Chemistry of Double-Bonded Functional Groups* (S. Patai, Ed.), p. 1. Wiley, London 1977.

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