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Effect of the Orientational Disorder on the Observed Geometry of Carboxylic Group in Dimers of Carboxylic Acids in Crystalline State*

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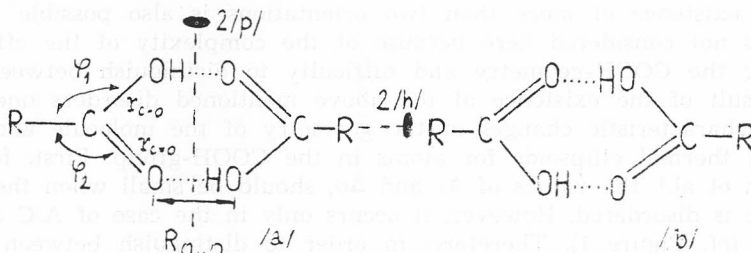
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Joint considerations of twofold symmetry axes producing various orientations of carboxylic groups and of non-coplanarity of these groups in a dimer lead to a new classification of orientational disorder in crystals of cyclic dimers of carboxylic acids.

Analysis of the geometry and particularly of the anisotropic thermal parameters of carboxylic atoms allows one to distinguish between the possible types of orientational disorder. Influences of dynamic disorder and mesomeric effects are discussed as well.

INTRODUCTION

The orientational disorder in the crystals of carboxylic acids results from a possible existence of the $(RCOOH)_2$ dimers in two orientations in which COOH groups are mutually related by a twofold axis^{1,2}.



For a planar dimer, form (a) may be transformed into form (b) by applying one of the two twofold axes of symmetry, $2(h)$ or $2(p)$, both lying in the plane of the dimer. As a consequence the observed bond lengths for $C=O$ and $C-OH$ as well as angles φ_1 and φ_2 are averaged over all unit cells in

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the crystal. Hence Dieterich et al.³ applied $\Delta r = r(\text{C—OH}) - r(\text{C=O})$ and $\Delta\varphi = \varphi_2 - \varphi_1$ as a measure of an orientational disorder: these two quantities are mutually correlated. The mesomeric effect and dynamic disorder of the proton should cause the same changes in the geometry of COOH group and additionally lead to a dependence between Δr and $R_{\text{O...O}}$.⁴ This kind of dependence was however, not observed⁴.

The aim of this paper is to show the consequences of noncoplanarity of COO planes in COOH groups in dimers of carboxylic acids in crystals on the orientational disorder of carboxylic group and, in turn, on the observed geometry of this group in crystals of these compounds.

DIFFERENT KINDS OF ORIENTATIONAL DISORDER — A MODEL

The picture of an orientational disorder is more complex due to the fact that the planes of two carboxyl groups in a centrosymmetric dimer are not necessarily coplanar, with a perpendicular distance between them, d (called hereafter a »step«) of about 10—40 pm.⁵ Due to the low energy sufficient to produce a »step«⁶, it may but need not exist in crystals. However, the presence of the above-mentioned displacement (step) implies two additional types of orientational disorder, as presented in Figure 1.

In a general case when the dimer forms a »step«, the two axes, called 2(h) and 2(p), produce different orientations, C and D, as presented in Figure 1. However, in general, one more orientation (B) may be produced by using a twofold axis of symmetry perpendicular to the planes of the COOH-groups assigned 2(v) (i. e. the action of 2(h) and 2(p) axes). The 2(h), 2(p) and 2(v) are crossed in the centre of symmetry.

If the lattice energies of two orientations are roughly comparable, then during the crystallization they may both build up the crystal and the crystal structure exhibits an orientational disorder. The following possibilities should be taken into account A/B (transformation of A by 2(v)), or A/C (transformation of A by 2(h)) or A/D (transformation of A by 2(p)). The action of the axes is not a physical fact existing in the crystal but it only represents the relationship between different orientations of the dimer of carboxylic acid.

The existence of more than two orientations is also possible but this case was not considered here because of the complexity of the effects influencing the COOH-geometry and difficulty to distinguish between them. As a result of the existence of the above mentioned disorders one should observe characteristic changes of the geometry of the molecule and of the shape of thermal ellipsoids for atoms in the COOH-group. First, following Dieterich et al.³, the values of Δr and $\Delta\varphi$, should be small when the crystal structure is disordered. However, it occurs only in the case of A/C and A/D disorder (cf. Figure 1). Therefore, in order to distinguish between various kinds of disorder, a few other parameters are introduced. Note as a result of the disorder of type A/B and A/C the »step« should be diminished whereas for A/D it should remain unchanged.

However, as a result of diminishing the step by the disorders of A/B and A/C type, the thermal motion vectors perpendicular to the COO-planes have to increase. Hence, very helpful parameters in analyzing the disorder of carboxylic groups are the lengths of the vectors of thermal motion for oxygen atoms in carboxylic groups calculated in two directions:

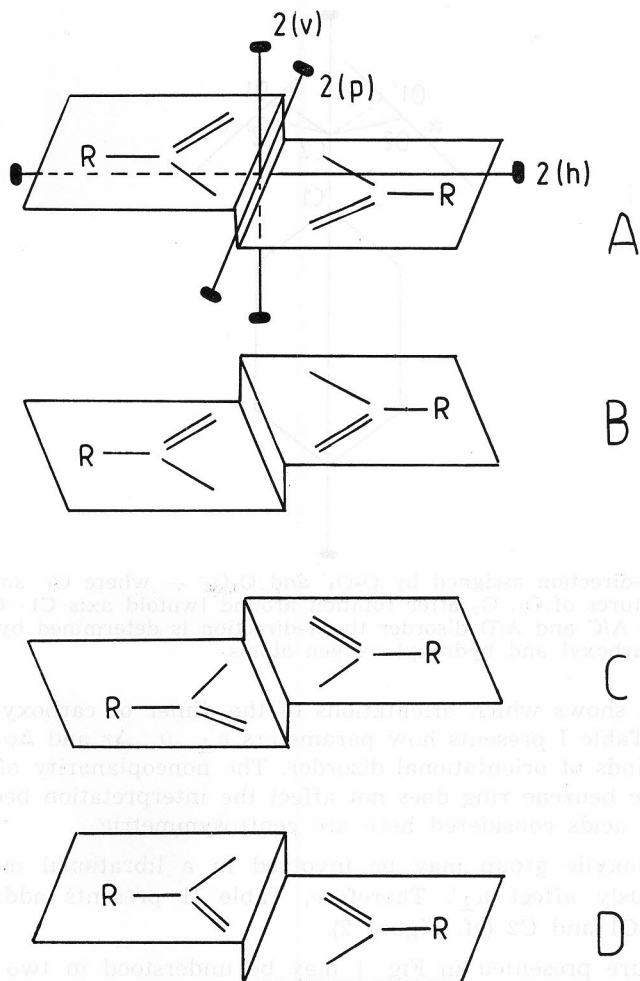


Figure 1 — Possible orientations of carboxylic groups in dimers of carboxylic acids if the step is taken into account; types of orientational disorder.

(i) perpendicularly to the COO-plane, assigned u_{\perp} , and
 (ii) coplanarly to the COO-plane, calculated in the direction given by the positions of oxygen atoms O_1O_2' or $O_1'O_2$, as shown in Figure 2 and called u_{\parallel} .
 If the carboxyl group in Figure 2 is rotated around the twofold axis (the effect of the action of $2(p)$ and $2(h)$ axes), the oxygen atoms O_1 and O_2 are transferred into positions O_1' and O_2' . The situation occurs in the case of the disorders of A/C and A/D type and should enlarge the u -value in this direction i. e. u_{\parallel} . The higher is the degree of A/C or A/D type of disorder, the smaller are the O_1O_2' or $O_1'O_2$ distances, but directions $O_1'O_2$ and $O_1'O_2'$ remain unchanged. The rotation axis of the COOH-group goes through the C1 and C2 carbon atoms (Figure 2).

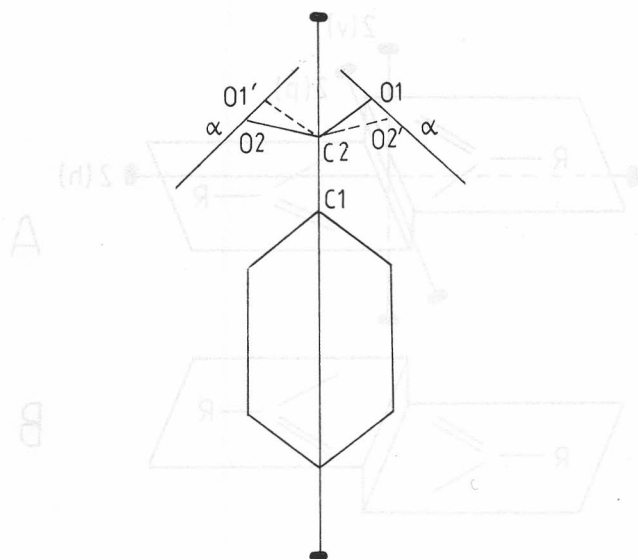


Figure 2 — α -direction assigned by $O_2O_{1'}$ and $O_1O_{2'}$ — where $O_{1'}$ and $O_{2'}$ are the pictures of O_1 , O_2 after rotation around twofold axis $C1-C2$. In the case of A/C and A/D disorder the α -direction is determined by two possible positions of carboxyl and hydroxyl oxygen atoms.

Figure 1. shows which orientations of the dimer of carboxylic acid may occur while Table I presents how parameters u_{\perp} , u_z , Δr and $\Delta\varphi$ are affected by various kinds of orientational disorder. The noncoplanarity of the COOH-group and the benzene ring does not affect the interpretation because dimers of carboxylic acids considered here are centrosymmetric.

The carboxylic group may be involved in a librational motion, which would obviously affect u_{\perp} . Therefore, Table II presents additionally the u -values for C1 and C2 (cf. Figure 2).

The picture presented in Fig. 1 may be understood in two ways. First, the action of symmetry operation is applied to the whole $(RCOOH)_2$ -units. The other is, as found by Bernstein and Leiserowitz⁷ that in some cases (e. g. trans-trans muconic acid) the above mentioned procedure should be applied only to the COOH-groups involved in a dimer. In other words, the disorder in this case does not need any symmetrical property of the R-group and is carried into effect by two rotationally different orientations of COOH-groups. Thus, the use of the C1—C2 direction during the construction of the A/C and A/D types of disorder seems to be proper (the disorder concerns only COOH groups).

Table 2 shows different kinds of orientational disorder for some derivatives of benzoic acid. Calculations of u_{\perp} and u_z , as well as d , $\Delta\varphi$ and Δr were carried out only for structures solved with very high precision, when e. s. d. for bond lengths ≤ 0.3 pm. The dynamic disorder and mesomeric effect are also discussed.

TABLE I

Influence of the type of disorder on values of parameters describing variation in geometry of COOH in dimers

	u_{\perp}^{\S}	u_z	Δr	$\Delta\varphi$	step
A/B	+	0	0	0	—
A/C	+	+	—	—	—
A/D	0	+	—	—	0
mesomeric effect	0	0	—	—	unknown

designations

0 no influence

— a decrease of the magnitude of parameter due to the disorder or mesomeric effect

+ an increase of the magnitude of parameter due to the disorder

§ for oxygen atoms, C1 and C2

u_{\perp} and step are influenced by a proper type of disorder if the step exists in a single dimer

TABLE II

Types of disorder for structures of benzoic acids

Designations

m — mesomeric effect

d — »step«

C1 — carbon atom in benzene ring

C2 — carbon atom in carboxylic group

O1 — carbonyl oxygen atom

O2 — hydroxy oxygen atom

The composition of the components of tensors of thermal motion is as follows (columns C2, O2, O1, C1):

first row — components u_{\perp}

second row — components u_z (for O1 and O2)

third, fourth and fifth rows — the lengths of axes of thermal motion ellipsoide tensor components, d, Δr and R_{\dots} are in pm $\times 10$, $\Delta\varphi$ in degrees

Structure	Δr	$\Delta\varphi$	C2	O2	O1	C1	d	R_{\dots}	effect	
1. <i>p</i> -hydroxy (20)	94	8.5	160	183	183	159	170	2658	lack	
				187	174					
				211	211	185				
				93	94	95				93
2. <i>p</i> -nitro (21)	68	5.7	181	187	183	179	190	2660	lack	
			150	174	172	149				
				126	162					
				183	201	202				181
3. 2,4-dinitro (22)	58	5.8	140	175	169	136	110	2656	lack	
				160	163					
				187	188	196				181
				108	110	110				106
4. <i>p</i> - <i>n</i> -butoxy B (23)	51	5.1	142	172	170	139	13	2652	lack	
				139	173					
				185	201	206				182
				116	120	108				110
			135	147	152	132				

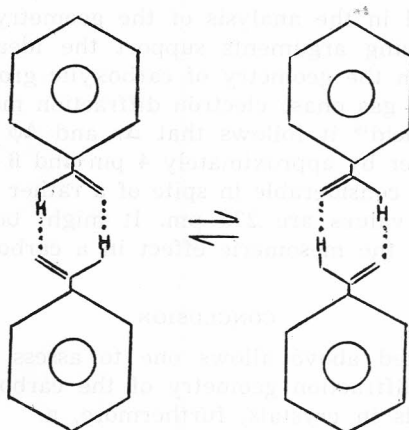
TABLE II to be continued

TABLE II continued

5. pentafluoro (24)	50	4.3	166	191	187	160	96	2668	lack
				178	217				
			216	253	250	209			
			117	125	117	116			
6. <i>p</i> -chloro (25)	36	3.4	228	277	257	221	0	2618	A/B and m
				202	122				
			236	283	269	228			
			113	113	118	112			
7. <i>p</i> -methoxy (26)	34	3.0	231	272	272	216	123	2632	A/C
				175	224				
			245	285	285	229			
			110	107	111	109			
8. <i>p</i> -fluoro (27)	31	3.1	177	206	198	171	24	2618	m
				186	185				
			208	209	218	205			
			157	162	158	150			
9. <i>p</i> -etoxy (28)	31	1.9	220	225	259	206	1	2600	A/C
				248	249				
			234	271	275	219			
			57	59	58	54			
10. benzoic (29)	10	0.9	203	234	231	196	131	2627	A/C
				216	168				
			212	242	237	211			
			99	101	105	100			
11. <i>p-n</i> -butoxy A (23)	9	1.3	130	157	159	122	48	2600	A/D or m
				184	166				
			186	204	202	180			
			124	137	136	117			
12. 2,3-dimetoxy (30)	7	1.4	147	178	178	143	85	2631	m
				163	189				
			168	188	191	161			
			112	117	121	108			
13. 2,5-dinitro (31)	12	2.2	128	153	149	123	23	2621	m
				156	113				
			141	160	158	142			
			109	105	108	100			
			127	148	146	122			

DYNAMIC DISORDER

It should be noted that orientations of molecules in an orientational disorder are fixed, whereas in the case of dynamic disorder, due to the motion of protons, there is a dynamic equilibrium (tautomeric equilibrium) between two orientations:

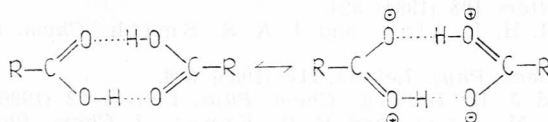


This equilibrium may be realized by either a 180° flip about the C...C vector⁸ or a concerted two proton jump⁹⁻¹¹. Attempts were made to decide which of these two mechanisms really works¹² but the conclusions do not seem to be quite decisive^{13,14}. Independently of the mechanism of proton transfer, the observed effect is expressed by an X-ray picture of COOH-geometry as a shortening of the C—OH bond and lengthening of the C=O bond. In other words, the Δr -value in this case is diminished. The same is observed for $\Delta\varphi$. Hence, as a result of a dynamic disorder of proton, the step cannot be cancelled out and this is indistinguishable from an orientational disorder of A/D-type. It seems that the dynamic disorder should not affect the u -values, but it should cause an increase of u_n since positions of oxygen atoms may depend on the positions of protons. This type of disorder seems to be preferred when the H-bond is strong i. e. when the $R_{O...O}$ -distance is short.

The solid state NMR-studies of p-toluic and terephthalic acids¹⁵, as well as of benzoic acid¹⁶, fully confirm the above picture. From the data of Meier et al. it was found that an increase of $R_{O...O}$ from 260.8(6) pm (terephthalic acid) to 262.7(1) pm (benzoic acid) is associated with an increase of activation energy of tautomerization from 2.6 kJ/mol to 4.9 kJ/mol. However, it should be taken into account that depending on the temperature of X-ray measurement a static orientational disorder may be transformed into a dynamic transfer of protons. This situation, however, cannot be decided by X-ray determination of the molecular geometry.

MESOMERIC EFFECT

The mesomeric effect on the geometry of COOH-group may be described by two main resonance structures participating in the description of the carboxylic group in dimers:



As a result, both $\Delta\varphi$ and Δr should decrease, in an extreme case to zero if both structures contribute equally. However, the possible influence of the COOH group is not usually taken into account^{4,17}. In our opinion, this effect

should not be rejected in the analysis of the geometry of the COOH group in dimers. The following arguments support the idea of the existence of mesomeric effect. From the geometry of carboxylic groups of monomers and dimers taken from the gas phase electron diffraction measurements for acetic acid¹⁸ and propionic acid¹⁹ it follows that Δr and $\Delta\varphi$ diminish while going from monomer to dimer by approximately 4 pm and 6° , respectively.

These changes are considerable in spite of a rather weak H-bond in these systems: their $R_{O\dots O}$ values are 270 pm. It might be assumed that for a shorter $R_{O\dots O}$ distance the mesomeric effect in a carboxylic group would be even stronger.

CONCLUSION

1. The model presented above allows one to assess the reliability of the X-ray measured diffraction geometry of the carboxylic group in dimers of carboxylic acids in crystals; furthermore, a
2. joint application of structural parameters: d , u_\perp , u_σ , $\Delta\varphi$ and Δr allows classification of orientational disorders into three kinds (Table I) or points to the mesomeric effect as being responsible for the small differences between C=O and C—OH bond lengths. The results of this kind of analysis, for highly precise X-ray measurements of the geometry of several carboxylic acids in crystals, are presented in Table II.
3. No conclusion can be made about the dynamic disorder of protons, except for the similarity of the geometry of carboxylic group for the dynamic disorder as well as for the mesomeric effect: small differences between C=O and C—OH bond lengths.

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SAŽETAK

Učinak orijentacijskog nereda na geometriju karboksilnih skupina u dimerima karboksilnih kiselina u kristalnom stanju

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Istodobno razmatranje dvostrukih simetrijskih osi, koje dovode do različitih orijentacija karboksilnih skupina, kao i njihove ne-koplanarnosti u dimeru dovodi do nove klasifikacije orijentacijskog nereda u kristalima cikličkih dimera karboksilnih kiselina. Analiza geometrije i, posebice, anizotropnih toplinskih parametara omogućuje razlikovanje mogućih tipova orijentacijskog nereda. Također je razmotren utjecaj dinamičkog nereda te mezomerijski učinci.