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Temperature-Dependent Order-Disorder Phenomena in Crystal Structures Containing Dimers of Carboxylic Acids: The Crystal and Molecular Structure of 3,5-Dinitrobenzoic Acid at Room and Liquid Nitrogen Temperature and Statistics of the Geometries of Hydrogen-Bonded Carboxyl Groups

Jan A. Kanters*, Jan Kroon, Rob Hooft, Arie Schouten,
Jack A. M. van Schijndel, and Jeroen Brandsen

Bijvoet Center for Biomolecular Research, Laboratory for Crystal and Structural Chemistry, Rijksuniversiteit Utrecht, Padualaan 8, 3584 CH, Utrecht, The Netherlands

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3,5-dinitrobenzoic acid crystallizes in space group $P2_1/c$ with four molecules in the unit cell. At room temperature (RT), the cell dimensions are $a = 10.0237(4)$, $b = 8.8728(3)$, $c = 9.5090(4)$ Å, $\beta = 95.68(1)^\circ$ and $V = 841.56(6)$ Å³ and at liquid nitrogen temperature (LNT) $a = 9.761(2)$, $b = 8.9192(4)$, $c = 9.444(2)$ Å, $\beta = 97.55(1)^\circ$ and $V = 815.1(2)$ Å³. At both temperatures, the crystals contain the common centrosymmetric carboxylic acid dimers. At RT the carboxyl groups are partially disordered, as indicated by the C=O [1.249(3)] and C-O [1.276(2)Å] distances, C-C=O [118.4(2)] and C-C-O [116.4(2)^o] angles and by the presence of disordered H atoms with occupancy factors of 0.63 and 0.37 in the O---O hydrogen bond.

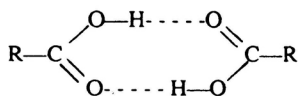
At LNT, the acidic proton is ordered with a distance of 0.96(2) Å from the donor hydroxyl O atom and the carboxyl group geometry is normal, with C=O 1.232(2) and C-O 1.305(2) Å and C-C=O 120.6(1) and C-C-O 114.4(1)^o.

The differences Δr distances and $\Delta\phi$ of the C-C-O angles are 0.027 Å and 2.0^o, respectively, at RT and 0.073 Å and 6.2^o, respectively, at LNT, which indicates an increase of ordering with decreasing temperature. The mechanism of disordering most probably invokes a temperature-dependent concerted two-proton jump across the dimer hydrogen bonds. To test the relationship between Δr and $\Delta\phi$, a statistical analysis is performed on the C-O distances and C-C-O angles of RT and LNT dimer and non-dimer structures retrieved from the Cambridge Structural Database. The analysis indicates that disorder in RT dimers is more frequent than in RT non-dimers and also that ordering is pronounced in both LT dimer and non-dimer structures.

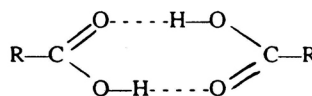
* To whom correspondence should be addressed.

INTRODUCTION

Numerous carboxylic acids are known to form dimeric, hydrogen-bonded dimers in the gas phase as well as in liquids and solids.^{1,2} From a great number of crystal structure analyses it appears that the great majority of dimers is symmetric and that only a limited number occur as asymmetric dimers (see Discussion for details). Consideration of formal bond diagrams³ and geometries from crystal structures without orientational disorder² have led to the following geometric features of the carboxyl group: C—O 1.31, C=O 1.21 Å, C—C—O 112 and C—C=O 122 and O—C=O 123°. However, it has been recognized for many years^{3,4,5,6} that experimental results of carboxylic acid dimers very often do not agree with these expected values. Although the sum of C—O distances never differs greatly from 2.53 Å, their difference Δr is often less than 0.10 Å, going down to zero, and the difference of the C—C—O angles $\Delta\phi$ displays a range from 10 to 0°. Interestingly, the hydrogen-bond distance O---O has as narrow distribution around the average of 2.65 Å.⁷ Several authors have studied the relation between Δr and $\Delta\phi$ and Dieterich, Paul and Curtin⁸ were among the first to report a plot of $|\Delta r|$ against $|\Delta\phi|$ values of 13 aromatic carboxylic acids. They found a good correlation that approaches a slope of 88 °Å⁻¹ as the differences approach zero. A more extensive analysis was performed by Borthwick⁹ on a sample of 50 structures, associated with the γ -aminobutyric acid and L-glutamic acid neurotransmitter systems, which contained 70 COO⁻ or COOH groups and the Δr , $\Delta\phi$ plot showed a good correlation with a slope of about 100° Å⁻¹. The relation between Δr and $\Delta\phi$ values has been explained in terms of orientational disorder of the carboxyl groups for which several mechanisms have been proposed. One mechanism is a state of static disorder² involving the existence of two dimer orientations (Ia and Ib) and, dependent on their relative proportions the observed carboxyl-group geometry will display increasing equalization of C—O bonds and C—C—O angles and disorder of the H atoms.



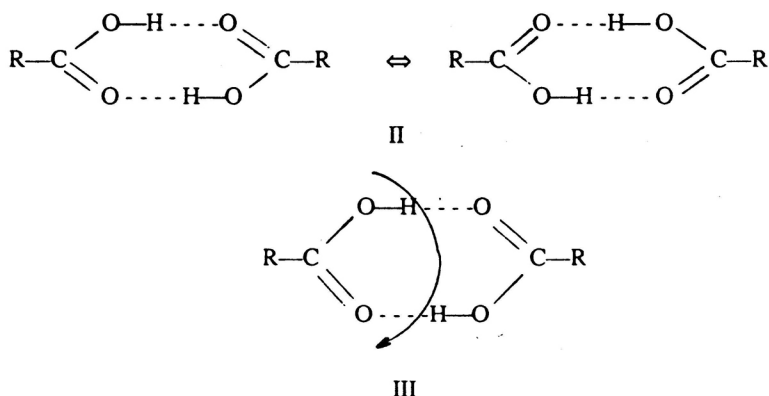
I(a)



I(b)

The alternative mechanism involves a dynamic model, the interpretation of which has raised some controversy in recent years.¹⁰ The following two mechanisms have been proposed: a) concerted two-proton exchange across the hydrogen bond^{11,12,13,14} (II) and b) a model in which the eight-membered hydrogen-bond ring performs a 180° flip about the C---C vector (III).¹⁵

The first model invokes a delocalized proton, either centrally located in a symmetric O---H---O hydrogen bond², which implies C—O bonds in a state of resonance, or undergoing rapid oscillations across the hydrogen bond causing interconversion between the C—O(H) and C=O bonds. Leiserowitz² has pointed out that the symmetric location of the proton is incompatible with the observation of a distinct C—O stretching mode in IR spectra of acids having C—O bonds of equal length. Also, symmetric O---H---O bonds have appreciably shorter distances (<2.50 Å)³ than those observed in cyclic dimers (see Discussion). The dynamic flip model b) (III) has been a subject of discussion in the literature. However, on the basis of a variety of experiments, including solid



state NMR¹¹, ¹⁷O quadrupole double resonance¹⁰, NMR relaxation¹⁶ and neutron scattering¹⁷, preference was given to the two-proton exchange model. Another argument in favour of this model is the consideration that the complete rotation of the eight-membered dimer ring in a crystal may give rise to considerable steric hindrance¹⁸, which would lead to activation energies appreciably higher than those measured.^{11,18}

X-ray and neutron diffraction techniques offer a suitable tool for accurately determining the geometries of acid dimers. Geometries have been reported² for a large number of acids. Of particular interest are the geometries of dimerized acids at different temperatures, from which reliable information about the temperature dependence of the proton exchange can be obtained. In the literature only a few examples have been reported, *viz.* benzoic acid³ and fluoromalonic acid^{19,20} (single crystal X-ray diffraction) and terephthalic acid²¹ (neutron powder diffraction). The results of a very accurate analysis of benzoic acid³ showed that at RT the dimer was nearly completely disordered, with an averaged carboxyl group with C-O distances of 1.258(2) and 1.268(2) Å and C-C-O angles of 118.7(1) and 117.8(1)° and the acidic hydrogen atom appearing as two 'half' atoms on the hydrogen bond at about 0.90 Å from each O atom. These results were interpreted as a random occurrence of the two tautomers I(a) and I(b) in nearly equal proportion. A single crystal neutron study at RT and 130 K gave unsatisfactory results, though they were reported not to be inconsistent with a disordered structure. A further neutron powder-profile study of deuterated *d*₅-benzoic acid at 5 K was generally consistent with an ordered structure, whereas at 130 K the results were less satisfactory and did not allow but to presume a probable disorder of some degree. It is unfortunate that no LT X-ray analysis was attempted using the same (RT) crystal which very probably would have given more reliable, comparable results. Neutron powder diffraction of deuterated terephthalic acid has been performed at five temperatures, ranging from 2 K to 300 K.²¹ Two neutron sources, a high-flux reactor source(HRS) and an intense pulsed spallation source (IPNS) were used. The RT structure(HRS) displayed equal C-O lengths [1.255(9) and 1.259(9) Å] but different C-C-O angles [116.3(6) and 119.0(6)°], which seems to be in conflict with the expected $\Delta r/\Delta\phi$ relation. Moreover, at 82 K both C-O bonds increase, to 1.294(10) and 1.272(10) Å, respectively, which is unprecedented, whereas at 2 K the distances are restored to 1.268(8) and 1.248(9) Å and the angles to 114.8(6) and 120.7(5)°, indicating a partial ordering. The IPNS analysis at 15 K gave analogous results. Accordingly, at 300 K the acid hydrogen thermal ellipsoid is effectively centered, but at 2 and 82 K the longer C-O bond captures the acid hydrogen.

In a solid-state NMR analysis of deuterated *p*-toluic acid (except for the acid group), an asymmetric, double-minimum potential with $\Delta G = 1.0$ kJ/mol between the tautomeric forms was reported.¹¹ At RT the protons undergo a fast transfer at an exchange rate of $2 \times 10^{10} \text{ s}^{-1}$ and with decreasing temperature the protons become increasingly ordered without going through an order-disorder transition. In agreement with the RT NMR results, the RT X-ray analysis²² showed pronounced disorder with equal C–O bonds [1.272(8) and 1.275(8) Å] and C–C–O angles [118.8(6) and 118.3(6)°].

The only example of a single-crystal X-ray analysis at RT and LNT using the same crystal was performed with fluoromalonic acid.^{19,20} The RT structure has nearly equal C–O lengths [1.253(3) and 1.257(3) Å] and C–C–O angles [116.6(2) and 116.8(2)°] and a completely disordered acid hydrogen atom. At LNT the lengths are 1.221(2) and 1.292(2) Å and the angles 119.8(2) and 113.6(2)° and the hydrogen atom is ordered. In the analyses it was also shown that the disorder-order process is reversible.

In a recent RT X-ray analysis of 3,5-dinitrobenzoic acid (3,5-DNB), we came across carboxyl-group C–O distances and C–C–O angles showing only small differences, about 0.02 Å and 2°, respectively, and a disordered acid hydrogen atom. This result prompted us to repeat the analysis with the same crystal at liquid nitrogen temperature with the aim of getting information about the temperature dependence of the dimer disorder. Also, we undertook a statistical analysis of RT geometries of the carboxyl group in dimers, symmetric and asymmetric ones, as well as on acids that are hydrogen-bonded in some other way. Although only a limited number of LNT dimer and non-dimer structures have been reported, their geometries were also studied.

EXPERIMENTAL

A transparent block-shaped crystal of dimensions 0.70 x 0.65 x 0.25 mm, obtained by crystallization from a mixture of acetone and toluene, was used for data collection at liquid nitrogen temperature (LNT, 100 K) and room temperature (RT, 295 K). Details of the data collection and refinement are reported in Table I. Unit-cell dimensions for both studies were determined from the setting angles of 25 reflections by the SET4 method.²³ The intensities were corrected for L_p effects, but not for absorption. Three standard reflections measured every hour showed only significant changes during the process of data collection. The structure was solved by direct methods with SHELXS86²⁴ and refined by weighted full-matrix least-squares using SHELXL76²⁵ with anisotropic thermal parameters of non-H atoms.

In the LNT analysis all H atoms were located from difference syntheses and they were included in the refinement with individual isotropic thermal parameters. No disorder of the acid H atom could be detected in the LNT analysis. The final difference map showed electron densities ranging from 0.3 to 0.4 $e \text{ \AA}^{-3}$ in the middle of all C–C and C–N bonds.

In the RT analysis, the H atoms of the ring were included in the refinement at calculated positions (C–H 1.00 Å) and refined in the riding mode with a general isotropic thermal parameter. At this stage of refinement, a difference map revealed two maxima of about 0.4 $e \text{ \AA}^{-3}$, each at a distance of about 0.8 Å from the respective oxygen atoms of the carboxyl group. The refinement was continued with inclusion of two half H atoms and fixed thermal parameters. In the next step the population parameters, constrained to sum to unity, were refined and in the last cycles positional and population parameters, resulting in final occupancies of 0.63 and 0.37 and a common isotropic U value of 0.05(1) Å² of the disordered acid H atoms.

Scattering factors were taken from Cromer and Mann²⁶ and anomalous dispersion corrections from Cromer and Libermann.²⁷ The program package EUCLID²⁸ was used for the calculations of geometry and illustrations. All calculations were carried out on an in-house micro VAXII computer.

TABLE I
Crystallographic and refinement data

	formula C ₇ H ₄ N ₂ O ₆	
	$M_r = 212.12$	
	spacegroup <i>P</i> 2 ₁ / <i>c</i> (<i>Z</i> = 4)	
	diffractometer ENRAF-NONIUS CAD4	
	Zr-filtered Mo K α radiation	
	$\lambda = 0.71073 \text{ \AA}$	
	crystal dimensions 0.70 x 0.65 x 0.25 mm	
	$F(000) = 432$	
	$\mu = 1.68 \text{ cm}^{-1}$	
	scan mode $\omega - 2\theta$	
	scan angle $\omega = (0.79 + 0.35 \tan\theta)^\circ$	
	reflections for cell constants	
13.59 $\leq \theta \leq$ 19.52	25 ($^\circ$)	12.41 $\leq \theta \leq$ 19.63
RT	cell dimensions	LNT
10.0237(4)	<i>a</i> (\AA)	9.761(2)
8.8728(3)	<i>b</i>	8.9192(4)
9.5090(4)	<i>c</i>	9.444(2)
95.68(1)	β ($^\circ$)	97.55(1)
841.56(6)	<i>V</i> (\AA^3)	815.1(2)
1.674	D_c (g cm ⁻³)	1.729
60.52	$2\theta_{\max}$ ($^\circ$)	69.74
-14,14; -12,12; -13,13	<i>h,k,l</i> limits	-15,15; -14,0; -14,12
310, 034, 203	standard reflections, hr ⁻¹	205, 222, 402
10044	measured reflections	5745
2511	unique reflections	3321
0.032	R_{merge}	0.026
2001	observed reflections ($I > 2.5\sigma[I]$)	2720
0.032	final <i>R</i> value	0.042
0.060	final ωR value	0.038
146	number of parameters	152
0.58	goodness of fit <i>S</i>	0.55
0.002	maximum shift/error	0.05
0.001	average shift/error	0.01
0.40	maximum residual density(e \AA^{-3})	0.41
$[\sigma^2(F_o)]^{-1}$	weights	$[\sigma^2(F_o)]^{-1}$
0.0181 x 10 ⁻⁴	extinction parameter	---

DISCUSSION

Molecular Structure and Packing

The final atomic coordinates of the RT and LNT structures with equivalent isotropic thermal parameters are given in Table II*, the anisotropic thermal parameters in Table III and the bond distances and angles in Table IV. At both temperatures 3,5-DNB forms the common centrosymmetric hydrogen-bonded dimer with planar carboxyl groups at a perpendicular distance of 0.029(7)[RT] and 0.025(4) \AA [LNT]. Figure 1

* Tables of the observed and calculated structure factors, dihedral and torsion angles of the RT and LNT structures are deposited in the Editorial Office of the *Croatica Chemica Acta*, Marulićev trg 19, 41000 Zagreb, Croatia, and can be obtained upon request.

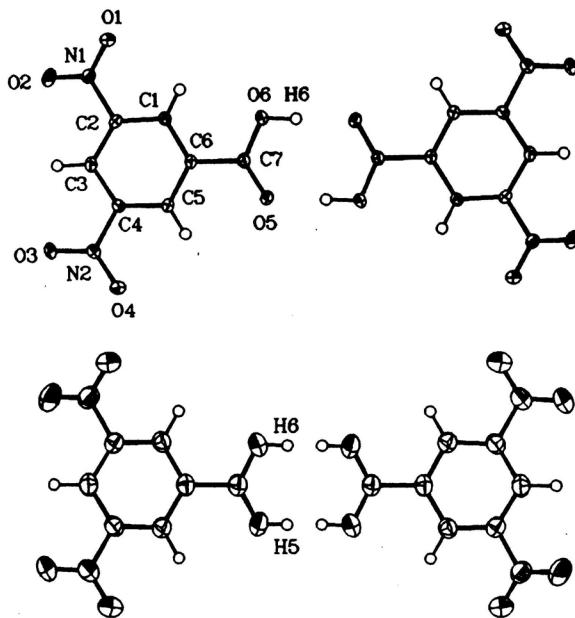


Figure 1. An ORTEP²⁹ drawing of the dimer structure at LNT (up) and RT (down). The thermal ellipsoids for non-H atoms are drawn at 50% probability.

shows a view of the dimer at RT and LNT with atom numbering. The two symmetry-related acid dimers in the unit cell are far from parallel, the interplanar angle of the dimer rings amounts to $42.5(2)^\circ$. These differently oriented neighbouring dimers are connected by two weak C—H...O hydrogen bonds (Table V), each involving an aromatic C—H donor and an oxygen atom of the N(1)O₂ nitro group as acceptor. As the donor H atom and the acceptor nitro group are at neighbouring carbon atoms of the phenyl ring, a ten-membered dimer ring is formed which connects the two acid dimer systems (Figure 2). The two dimer systems form a two-dimensional layer structure and the role of C—H...O interactions in determining the stacking of molecules² is nicely corroborated in the 3,5-DNB structure.

The angle between the planar phenyl ring and the carboxyl group is $7.33(11)^\circ$ at RT and $7.56(6)^\circ$ at LNT. The N(1)O₂ nitro group is rotated with respect to the phenyl ring, $23.9(1)^\circ$ at RT and $23.77(6)^\circ$ at LNT, while the N(2)O₂ group is coplanar with the phenyl ring at RT and LNT.

The RT and LNT carboxyl-group geometries show striking differences: at RT the C=O and C—O bonds are $1.249(3)$ and $1.276(2)$ Å, respectively, and the C—C=O and C—C—O angles $118.4(2)$ and $116.4(2)^\circ$, respectively, whereas at LNT the geometries approach those of an ordered carboxyl group with C=O $1.232(2)$, C—O $1.305(2)$ Å, C—C=O $120.6(1)$ and C—C—O $114.4(1)^\circ$.

The RT geometry is indicative of an appreciable degree of disorder and this was supported by the appearance of two distinct maxima of about $0.4 \text{ e } \text{Å}^{-3}$ at 0.80 Å of

TABLE II

Fractional coordinates and (equivalent) isotropic thermal parameters (\AA^2) with e.s.d.'s in parentheses for 3,5-dinitrobenzoic acid at RT (upper lines) and LNT (lower lines). * $U_{\text{eq}} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$
 ** population parameter 0.37; *** population parameter 0.63

	x	y	z	$U_{\text{eq(iso)}}^*$
O(1)	0.0754(2)	0.6516(2)	0.3760(2)	0.0586(7)
	0.07516(9)	0.6481(1)	0.3789(1)	0.0221(3)
O(2)	-0.0416(2)	0.4804(2)	0.2600(2)	0.0625(7)
	-0.04501(9)	0.4738(1)	0.2595(1)	0.0237(3)
O(3)	0.1879(3)	0.1986(2)	-0.0834(3)	0.100(1)
	0.1917(1)	0.1952(1)	-0.0802(1)	0.0420(4)
O(4)	0.3463(2)	0.3028(2)	-0.1831(2)	0.0590(6)
	0.34761(9)	0.3066(1)	-0.18483(9)	0.0206(3)
O(5)	0.4676(2)	0.8258(2)	-0.0724(2)	0.0529(6)
	0.46748(9)	0.8311(1)	-0.06878(9)	0.0191(2)
O(6)	0.3919(2)	0.9311(2)	0.1188(2)	0.0537(6)
	0.39018(9)	0.9307(1)	0.1249(1)	0.0200(3)
N(1)	0.0549(2)	0.5638(2)	0.2777(2)	0.0400(6)
	0.0540(1)	0.5591(1)	0.2795(1)	0.0156(3)
N(2)	0.2637(2)	0.3028(2)	-0.0984(2)	0.0474(7)
	0.2654(1)	0.3026(1)	-0.0976(1)	0.0190(3)
C(1)	0.2297(2)	0.6865(2)	0.1572(2)	0.0323(6)
	0.2304(1)	0.6848(1)	0.1605(1)	0.0135(3)
C(2)	0.1526(2)	0.5606(2)	0.1719(2)	0.0320(6)
	0.1529(1)	0.5571(1)	0.1743(1)	0.0132(3)
C(3)	0.1605(2)	0.4329(2)	0.0900(2)	0.0348(6)
	0.1613(1)	0.4299(1)	0.0921(1)	0.0146(3)
C(4)	0.2523(2)	0.4362(2)	-0.0084(2)	0.0343(6)
	0.2540(1)	0.4351(1)	-0.0066(1)	0.0140(3)
C(5)	0.3316(2)	0.5598(2)	-0.0299(2)	0.0331(6)
	0.3330(1)	0.5604(1)	-0.0273(1)	0.0136(3)
C(6)	0.3189(2)	0.6859(2)	0.0543(2)	0.0320(6)
	0.3203(1)	0.6859(1)	0.0573(1)	0.0132(3)
C(7)	0.3992(2)	0.8239(2)	0.0305(2)	0.0369(7)
	0.4001(1)	0.8237(1)	0.0325(1)	0.0147(3)
H(5)**	0.512(7)	0.900(9)	-0.086(7)	0.05(1)
	-	-	-	-
H(6)***	0.434(4)	1.010(6)	0.100(5)	0.05(1)
	0.441(2)	1.018(2)	0.103(2)	0.081(7)
H(11)	0.2218(2)	0.7765(2)	0.2191(2)	0.046(4)
	0.220(1)	0.768(2)	0.216(2)	0.016(4)
H(31)	0.1027(2)	0.3429(2)	0.1017(2)	0.046(4)
	0.108(1)	0.343(2)	0.105(2)	0.023(4)
H(51)	0.3961(2)	0.5585(2)	-0.1036(2)	0.046(4)
	0.392(1)	0.562(2)	-0.100(2)	0.020(4)

the O atoms in the O---O hydrogen-bond region in a difference synthesis based on F_{calc} computed with all atoms except the acidic hydrogen atom. The same procedure with the LNT data resulted in one, unsplit maximum of height 0.8 e \AA^{-3} .

TABLE III

Anisotropic thermal parameters at RT (upper lines) and LNT (lower lines).

	<i>U</i> (1,1)	<i>U</i> (2,2)	<i>U</i> (3,3)	<i>U</i> (2,3)	<i>U</i> (1,3)	<i>U</i> (1,2)
O(1)	0.068(1) 0.0266(5)	0.056(1) 0.0201(5)	0.057(1) 0.0215(5)	-0.0154(9) -0.0053(4)	0.0289(9) 0.0108(4)	-0.0093(9) -0.0030(4)
O(2)	0.043(1) 0.0166(4)	0.074(1) 0.0277(5)	0.073(1) 0.0278(5)	-0.005(1) -0.0015(4)	0.0189(9) 0.0070(4)	-0.0215(9) -0.0087(4)
O(3)	0.143(2) 0.0598(7)	0.061(1) 0.0269(6)	0.108(2) 0.0465(7)	-0.047(1) -0.0204(5)	0.072(2) 0.0340(6)	-0.061(1) -0.0289(5)
O(4)	0.074(1) 0.0242(5)	0.050(1) 0.0191(4)	0.058(1) 0.0203(5)	-0.0133(8) -0.0029(4)	0.027(1) 0.0097(4)	-0.0038(9) -0.0007(4)
O(5)	0.068(1) 0.0240(4)	0.046(1) 0.0168(4)	0.048(1) 0.0181(4)	-0.0038(8) -0.0010(4)	0.0232(9) 0.0090(4)	-0.0249(9) -0.0066(4)
O(6)	0.074(1) 0.0277(5)	0.0310(8) 0.0121(4)	0.059(1) 0.0221(5)	-0.0090(8) -0.0028(4)	0.0243(9) 0.0100(4)	-0.0180(8) -0.0055(4)
N(1)	0.037(1) 0.0145(5)	0.039(1) 0.0152(5)	0.045(1) 0.0179(5)	0.0041(9) 0.0021(4)	0.0119(8) 0.0048(4)	0.0006(9) 0.0010(4)
N(2)	0.063(1) 0.0238(5)	0.035(1) 0.0151(5)	0.046(1) 0.0189(5)	-0.0079(8) -0.0034(4)	0.013(1) 0.0059(4)	-0.0089(9) -0.0042(4)
C(1)	0.036(1) 0.0145(5)	0.027(1) 0.0113(5)	0.034(1) 0.0146(5)	0.0009(8) 0.0003(4)	0.0034(9) 0.0019(4)	-0.0011(8) 0.0004(4)
C(2)	0.032(1) 0.0113(5)	0.033(1) 0.0154(5)	0.032(1) 0.0132(5)	0.0035(8) 0.0019(4)	0.0052(8) 0.0030(4)	-0.0006(9) -0.0001(4)
C(3)	0.037(1) 0.0145(5)	0.031(1) 0.0137(5)	0.036(1) 0.0154(5)	0.0016(9) 0.0011(4)	0.0026(9) 0.0016(4)	-0.0076(9) -0.0036(4)
C(4)	0.041(1) 0.0163(5)	0.029(1) 0.0120(5)	0.033(1) 0.0138(5)	-0.0033(8) -0.0018(4)	0.0031(9) 0.0020(4)	-0.0033(9) -0.0013(4)
C(5)	0.036(1) 0.0136(5)	0.032(1) 0.0136(5)	0.032(1) 0.0138(5)	0.0017(9) 0.0013(4)	0.0050(9) 0.0024(4)	-0.0025(9) -0.0012(4)
C(6)	0.034(1) 0.0137(5)	0.029(1) 0.0119(5)	0.033(1) 0.0139(5)	0.0025(8) 0.0012(4)	0.0024(9) 0.0020(4)	-0.0041(8) -0.0016(4)
C(7)	0.045(1) 0.0165(5)	0.031(1) 0.0122(5)	0.036(1) 0.0154(5)	0.0011(9) 0.0006(4)	0.008(1) 0.0022(4)	-0.0069(9) -0.0014(4)

Figure 3 portrays electron densities of the difference map in the plane of the dimer at RT and LNT.

Although the differences of the C–O lengths and C–C–O angles at RT are small [0.027 Å and 2.0°], it is obvious that the disordering is not complete. On the assumption that complete disordering requires Δr and $\Delta\phi$ ranging down to zero, the observed differences roughly indicate a 70–80% disordering, based on Δr and $\Delta\phi$ values of 0.10 Å and 10°, respectively, of LT geometries, which may be expected to be ordered to a high degree (see below under statistics). This geometry-based degree of disorder agrees well with the one that can be derived from the occupancy factor of H(6)[0.63] and of H(5)[0.37].

The observed geometries of bonds and angles involving the disordered hydrogen atoms are quite satisfactory: O(5)–H(5) 0.81(8), O(6)–H(6) 0.85(5) Å, C(7)–O(5)–H(5) 119(5), C(7)–O(6)–H(6) 115(3)°. Deviations of the H atoms from the carboxyl-group plane are small, 0.005 for H(5) and 0.053 Å for H(6). In the LNT structures these geometries are: O(6)–H(6) 0.96(2) Å, C(7)–O(6)–H(6) 111(1)° and the deviation of H(6) from the plane of the carboxyl group is 0.025 Å.

TABLE IV
Bond distances (Å) and bond angles (°)

	RT	LNT		RT	LNT
O(1)-N(1)	1.219(3)	1.226(1)	O(1)-N(1)-O(2)	124.5(2)	124.8(1)
O(2)-N(1)	1.216(3)	1.225(1)	O(1)-N(1)-C(2)	117.6(2)	117.70(9)
O(3)-N(2)	1.214(3)	1.222(2)	O(2)-N(1)-C(2)	117.9(2)	117.5(1)
O(4)-N(2)	1.211(3)	1.224(1)	O(3)-N(2)-O(4)	123.7(2)	124.3(1)
O(5)-C(7)	1.249(3)	1.232(2)	O(3)-N(2)-C(4)	117.3(2)	117.4(1)
O(6)-C(7)	1.276(2)	1.305(2)	O(4)-N(2)-C(4)	119.0(2)	118.4(1)
N(1)-C(2)	1.472(3)	1.474(2)	C(2)-C(1)-C(6)	118.4(2)	118.3(1)
N(2)-C(4)	1.472(3)	1.474(2)	N(1)-C(2)-C(1)	118.2(2)	117.9(1)
C(1)-C(2)	1.373(3)	1.383(2)	N(1)-C(2)-C(3)	118.7(2)	118.7(1)
C(1)-C(6)	1.389(3)	1.394(2)	C(1)-C(2)-C(3)	123.1(2)	123.3(1)
C(2)-C(3)	1.382(3)	1.383(2)	C(2)-C(3)-C(4)	116.4(2)	116.3(1)
C(3)-C(4)	1.376(3)	1.383(2)	N(2)-C(4)-C(3)	118.3(2)	118.2(1)
C(4)-C(5)	1.381(3)	1.386(2)	N(2)-C(4)-C(5)	118.3(2)	118.6(1)
C(5)-C(6)	1.389(3)	1.390(2)	C(3)-C(4)-C(5)	123.4(2)	123.2(1)
C(6)-C(7)	1.495(3)	1.490(2)	C(4)-C(5)-C(6)	117.9(2)	118.3(1)
O(5)-H(5)	0.81(8)	-	C(1)-C(6)-C(5)	120.7(2)	120.6(1)
O(6)-H(6)	0.85(5)	0.96(2)	C(1)-C(6)-C(7)	119.8(2)	120.3(1)
			C(5)-C(6)-C(7)	119.4(2)	119.1(1)
			O(5)-C(7)-O(6)	125.3(2)	125.0(1)
			O(5)-C(7)-C(6)	118.4(2)	120.6(1)
			O(6)-C(7)-C(6)	116.4(2)	114.4(1)
			C(7)-O(5)-H(5)	119(5)	-
			C(7)-O(6)-H(6)	115(3)	111(1)

TABLE V

Hydrogen-bond geometries (distances in Å, angles in degrees) at RT (upper lines) and LNT (lower lines). Symmetry operation is performed on the acceptor atom A: (i) $1-x, 2-y, -z$; (ii) $-x, 1/2 + y, 1/2 - z$; (iii) $-x, -1/2 + y, 1/2 - z$.

D-H...A	D...A	D-H	H...A	D-H...A
O(5)-H(5)...O(6 ⁱ)	2.637(2)	0.81(8)	1.83(8)	179(7)
O(6)-H(6)...O(5 ⁱ)	2.637(2)	0.85(5)	1.79(5)	175(5)
	2.630(1)	0.96(2)	1.67(2)	179(2)
C(1)-H(11)...O(2 ⁱⁱ)	3.357(3)	1.00(2)	2.58(2)	135(2)
	3.294(2)	0.92(1)	2.54(1)	139(1)
C(3)-H(31)...O(1 ⁱⁱⁱ)	3.475(3)	1.00(2)	2.49(2)	170(2)
	3.447(2)	0.95(1)	2.51(1)	168(1)

Statistics of the Geometry of the Carboxyl Group

In the introduction, the Δr against $\Delta\phi$ plots reported for a limited number of aromatic acids⁸ and aminoacid residues⁹ have already been mentioned. Now, a more extensive analysis will be presented with the aim to study the Δr , $\Delta\phi$ relationship of the carboxyl group in different types of hydrogen bonds. For this purpose a set of carboxyl-group containing X-ray and neutron diffraction structures with R-values ≤ 0.075 , excluding structures with transition metals and uncorrected errors, were retrieved from the

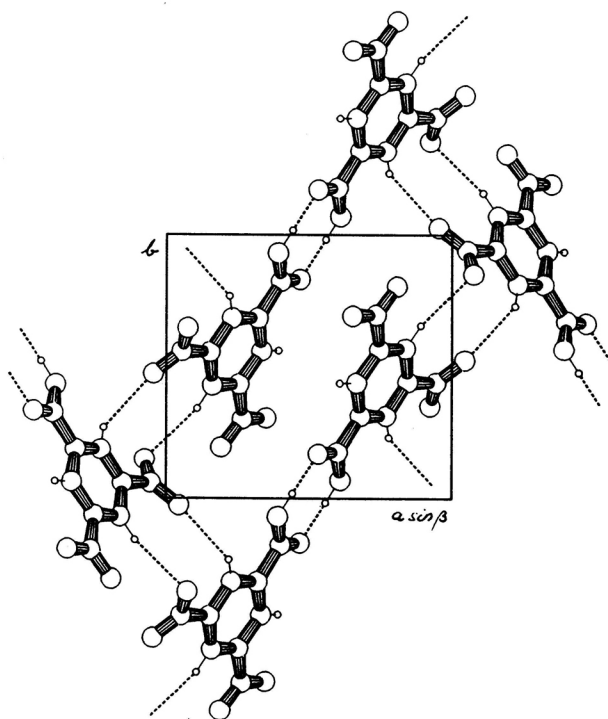


Figure 2. View of a part of the LNT structure along the c axis, showing the connection of the acid dimers by double-ribbon C-H...O hydrogen bonds.

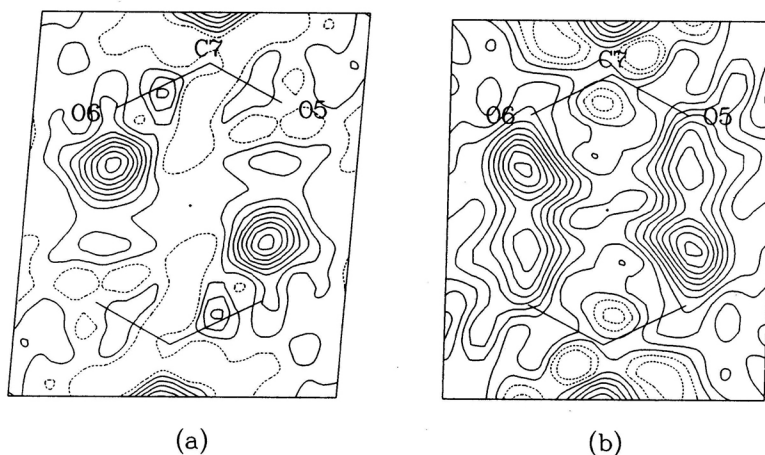


Figure 3. Difference Fourier synthesis in the plane of the carboxyl group of the LNT (Figure 2a) and RT (Figure 2b) dimer. The dashed line is the $-0.1 \text{ e}\text{\AA}^{-3}$ contour level. The interval between contour levels is $0.1 \text{ e}\text{\AA}^{-3}$ in Figure 2a and $0.05 \text{ e}\text{\AA}^{-3}$ in Figure 2b.

Cambridge Crystallographic Database.³⁰ In the case of multiple occurrence of a structure, the one with the lowest R-value was selected. The structures were divided into three classes with different types of hydrogen bonding, always involving the donor hydroxyl group and an oxygen acceptor, and within these classes a distinction was also made between RT and LT structures. The contributors to the six classes are as follows:

Class I consists of 295 RT (RTDIM) and 18 LT (LTDIM) symmetric dimers.

Class II consists of 19 RT (RTNSDIM) and only 2 LT (LTNSDIM) non-symmetric dimers.

Class III consists of 467 RT (RTNOD) and 45 LT (LTNOD) carboxyl groups involved in non-dimer type hydrogen bonding.

The plot of Δr against $\Delta\phi$ (Figure 4) of the RTDIM set has a slope of 97°\AA^{-1} and a correlation coefficient of 0.83. The few points with negative Δr and $\Delta\phi$ values arise from the bonding of the acidic hydrogen atom to the oxygen atom with the shorter C–O bond. Points with either negative Δr or $\Delta\phi$ values are also inconsistent but as the values are very small, these points relate to disordered bonds. The plot of the LTDIM set (Figure 5, slope $112^\circ \text{\AA}^{-1}$ and correl. coeff. 0.66) clearly shows that there is no disorder here as the average Δr and $\Delta\phi$ values are both large (0.093\AA and 11.2° , respectively). As Figure 6 (slope 79°\AA^{-1} and corr. coeff. 0.71) demonstrates, the RTNSDIM dimers, although small in number, have a range of $\Delta r/\Delta\phi$ ratios, which is not very different from the RT symmetric dimers (Figure 4). As it may be expected, the 4 carboxyl groups of the 2 LTNSDIM structures have large Δr and $\Delta\phi$ values, which average to 0.087\AA and 9.7° , respectively.

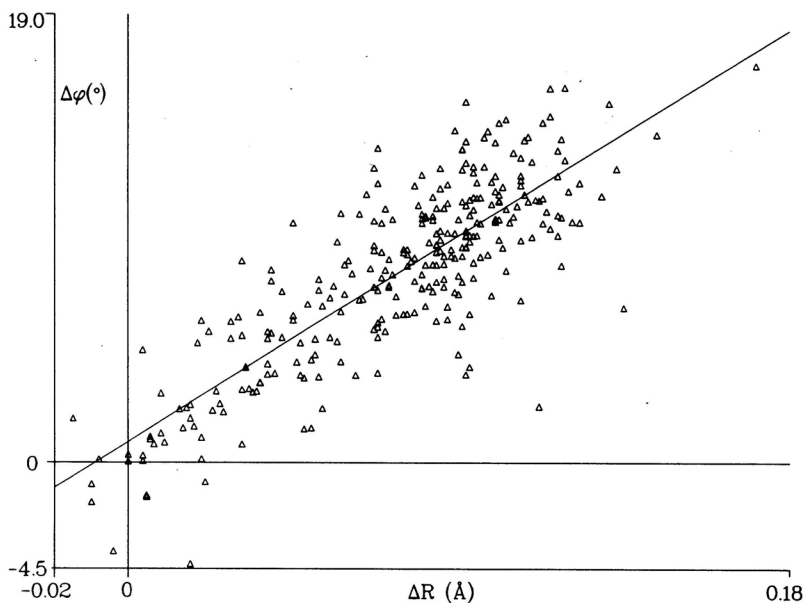


Figure 4. A plot of the difference in C–C–O angles ($\Delta\phi$) against the difference in C–O bond lengths (Δr) of the RTDIM set. $\Delta\phi$ is always taken as the difference between C–C=O and C–C–O(H), and Δr as the difference between C–O(H) and C=O. The regression line is also shown.

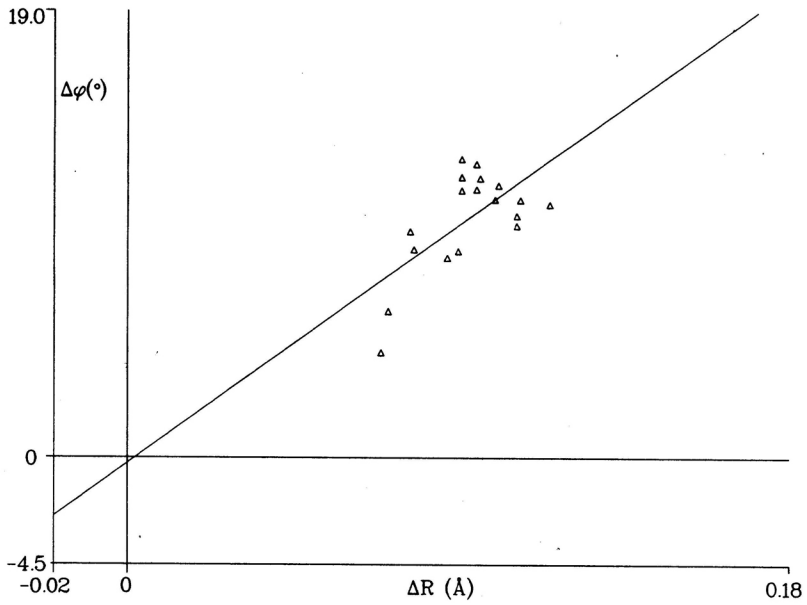


Figure 5. A plot of $\Delta\phi$ against Δr of the LTDIM set.

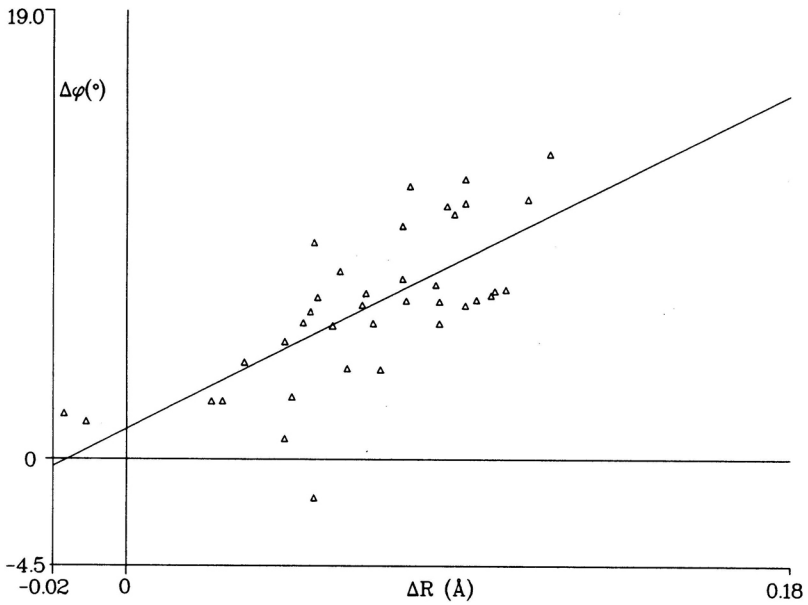


Figure 6. A plot of $\Delta\phi$ against Δr of the RTNSDIM set.

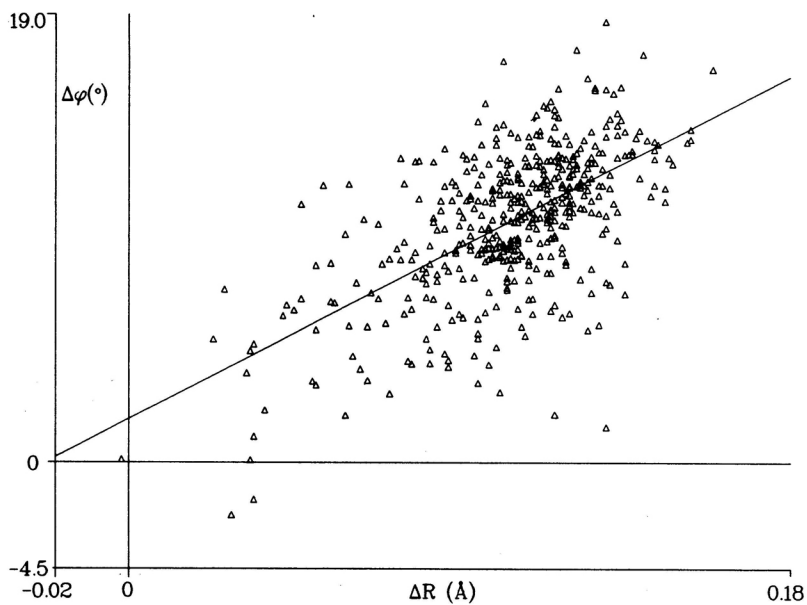


Figure 7. A plot of $\Delta\phi$ against Δr of the RTNOD set.

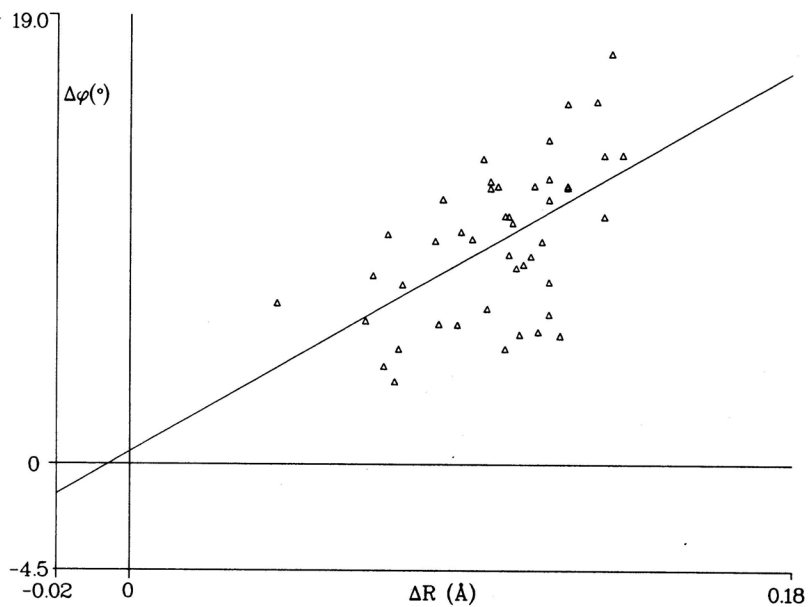


Figure 8. A plot of $\Delta\phi$ against Δr of the LTNOD set.

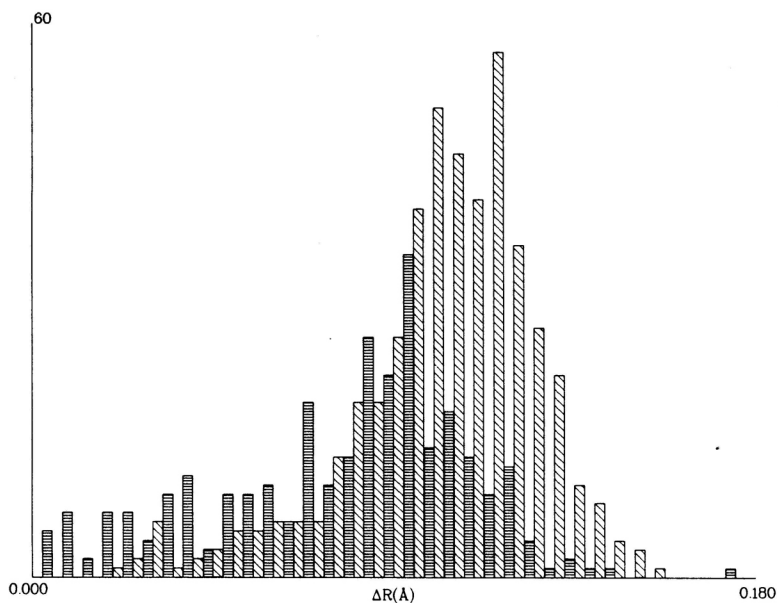


Figure 9. A composite histogram of Δr values of the RTDIM set (dashed horizontally) and of the RTNOD set (dashed diagonally).

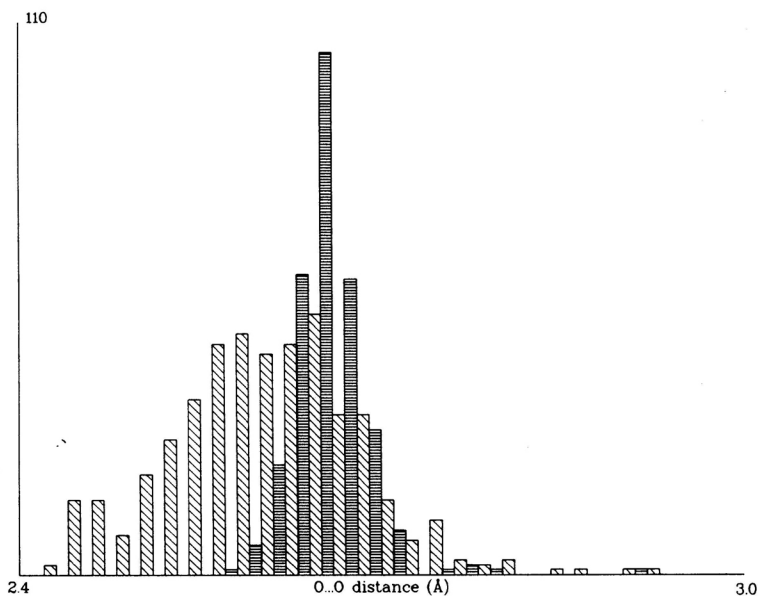


Figure 10. A composite histogram of the O...O distances of the RTDIM set (dashed horizontally; average O...O: 2.65(3) Å) and of the RTNOD set (dashed diagonally; average O...O: 2.61(8) Å).

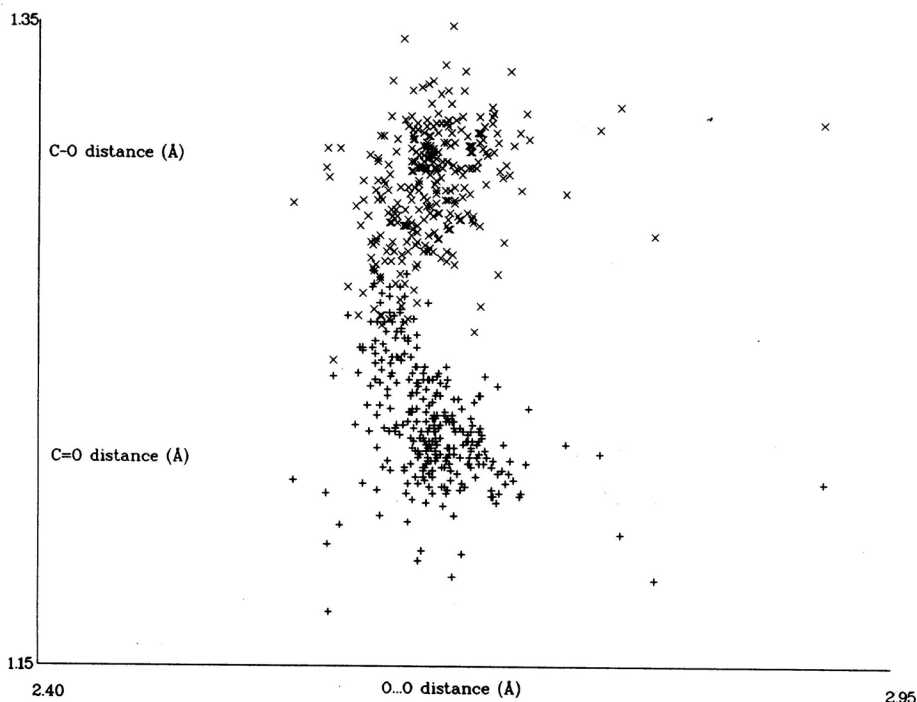


Figure 11. A plot of the C-O(H) [X] and C=O [+] distances against O...O distances of the RTDIM set.

Class III has the largest number of hydrogen bonds. The RTNOD structures that are of the non-dimer type give rise to a plot (Figure 7, slope $81 \text{ }^\circ\text{\AA}^{-1}$, correl. coeff. 0.61) which differs from that of the RTDIM set (Figure 4) in that the region with small Δr and $\Delta\phi$ values has relatively fewer contributors. The clustering in the region of larger values indicates that in non-dimerized carboxyl groups disorder is less manifest than in dimers, either symmetric or non-symmetric. As it can be seen, the plot of LTNOD set (Figure 8, slope $89 \text{ }^\circ\text{\AA}^{-1}$, corr. coeff. 0.57) seems to indicate that the degree of disorder is small in this type of hydrogen bonds and about the same as that observed in the LTDIM set.

A composite histogram of the Δr values of the RTDIM and RTNOD sets (Figure 9) shows that disorder is more frequent in dimers than in non-dimers and, accordingly, the average Δr value is smaller in dimers [0.076(3)] than in non-dimers [0.103(2) Å]. However, the non-dimer data should be treated with care. In an analysis of 200 carboxyl groups, Ichikawa⁷ has demonstrated that the much larger spread of O...O distances in non-dimers, as opposed to the very narrow O...O range in dimers (Figure 10), has a significant effect on the carboxyl-group geometry: the C=O distances and C-C-O angles decrease, and the C-O distances and C-C=O angles increase with increasing O...O distance. Although this effect parallels the disorder-order geometry relationship, it is of little importance in dimers because of the already mentioned small

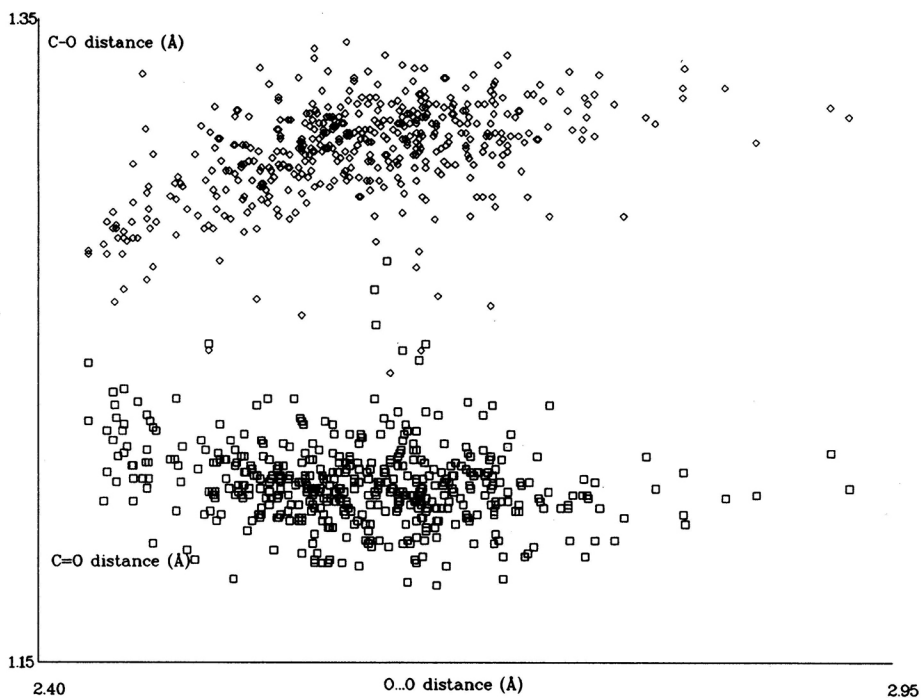


Figure 12. A plot of the C–O(H) [◇] and C=O [□] distances against the O...O distances of the RTNOD set.

O...O range. For comparison with the results of Ichikawa, the analysis was repeated for the larger RTDIM and RTNOD sets as to the dependence of C–O and C=O distances on O...O distances. In agreement with Ichikawa, the RTDIM plot (Figure 11) clearly demonstrates a poor correlation of both types of C–O distances and the O...O distance. Ichikawa's conclusion that dimers display a continuous degree of disorder is supported by our analysis. However, in contrast to Ichikawa's plot, the plot of the RTNOD set (Figure 12) does not bring out a significant increase of C–O and decrease of C=O distances with increasing O...O distance. Only at very short O...O distances such an effect might be present, as Figure 12 shows. Thus, as far as our sets are concerned, the geometry effect does not invalidate the conclusion that disorder in non-dimers is less frequent.

The main conclusion from the analysis is that a continuous degree of disorder is present in dimers which is significantly temperature-dependent, as comparison of RT and LT dimers indicates. The fact that disorder is more frequent in dimers may well indicate that the isolated hydrogen-bonded dimer system facilitates this transfer.

The 180° flip-over model, strongly advocated by Furic^{15,31,32}, is highly improbable because of steric limitations imposed by the crystal packing. For the LNT structure of 3,5-DNB this is convincingly demonstrated by a calculation of the energy barrier of rotation of the dimer ring system in the crystal surroundings. A rotation of about 90°

results in very short contacts between the carboxyl-group oxygen atoms, on the one hand, and oxygen atoms of the nitro group and nitrogen atoms, on the other, of 2.40 and 1.90 Å, respectively, with an energy barrier of more than 200 kcal/mole. Thus, it is very probable that the disordering mechanism involves a dynamical, concerted two-proton transfer.

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SAŽETAK

Temperaturno ovisne pojave red-nered u kristalnim strukturama dimera karboksilnih kiselina: kristalna i molekulska struktura 3,5-dinitrobenzojeve kiseline na sobnoj temperaturi i temperaturi tekućeg dušika te statistika geometrija karboksilnih grupa premoštenih vodikovim vezama

J. A. Kanters, J. Kroon, R. Hooft, A. Schouten, J. A. M. van Schijndel i J. Brandsen

3,5-dinitrobenzojeva kiselina tvori kristale koji imaju simetriju karakteriziranu prostornom grupom $P2_1/c$. U jediničnoj ćeliji nalaze se 4 molekule. Dimenzije jedinične ćelije određene su pri sobnoj temperaturi kao i pri temperaturi tekućeg dušika. Pokazano je da kristal ima centrosimetrični dimer karboksilne kiseline kod obje temperature. Međutim, karboksilne skupine djelomice su neodređene pri sobnoj temperaturi. Utvrđeno je da se red povećava sniženjem temperature. Razmatran je mogući mehanizam postanka nereda.