Structures of Two Malonamide Derivatives as Models of Nylons *n*,3 and of Peptidomimetic Compounds

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ABSTRACT: We have synthesized and analyzed by X-ray diffraction two malonamide derivatives of the type $RNHCOCH_2CONHR'$, with R = R′ = phenyl or propyl. We have compared their structure with other known compounds of the same family. In all cases the planes of the peptide groups are approximately perpendicular, as a result of the fact that the two ψ torsion angles about the carbonyl–methylene bonds are in the range 100–150°. An intramolecular hydrogen bond is never found. Due to this conformation, a network of hydrogen bonds oriented in two directions in space is formed, a situation also found in *n*,3 nylons. The propyl derivative is thus an excellent model for these types of nylons. These results also allow a better understanding of malonamide conformation in peptidomimetic compounds.

Introduction

Malonamide derivatives are of interest in two respects: as monomers in the nylon *n*,3 family and as components in peptidomimetic substances. The *n*,3 nylons have not been studied in great detail. A model for their structure has been proposed by Paiaro et al.[1] However, work in our laboratory indicates[2] that *n*,3 nylons are polymorphic and may have different structures depending on the mode of sample preparation.

Malonamide derivatives have been widely used in peptidomimetic compounds.[3] The structures of some of them have been studied by X-ray diffraction.[4–7] Their conformations have been analyzed by computational methods[8–11] with conflicting results, which will be analyzed in this paper.

In view of this situation we decided to synthesize and analyze the X-ray structures of two malonamide derivatives: *N*,*N*′-diphenylmalonamide and *N*,*N*′-dipropylmalonamide. Their schematic structure is shown in Figure 1. These two compounds were chosen because inspection of the literature showed that most malonamide derivatives which had been crystallized[5,7] either had substituents in the central methylene group or more than one substituent in one or both of the nitrogens, so that one or both peptide groups could not form hydrogen bonds. Another family of malonamide derivatives which had been previously studied has the central malonamide unit intact, but additional residues forming hydrogen bonds are present,[4,6] which may interfere with the conformational preference of the malonamide units inserted in a polymer.

An analysis of the structures of the simple compounds chosen by us gives an insight on the structural preferences of malonamide derivatives both in nylon *n*,3 polymers and in peptidomimetic compounds.

Experimental Section

Synthesis. Synthesis of *N*,*N*′-Diphenylmalonamide. This compound was obtained by bubbling distilled carbon suboxide (a ketene whose structure is O=C=C=C=O) into a xylene solution of aniline. Carbon suboxide was prepared by thermal decomposition of malonic acid in the presence of phosphorus pentoxide.[12]

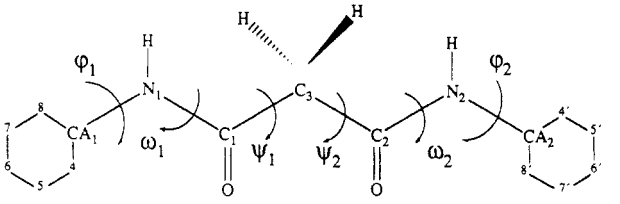

Figure 1. Atomic numbering scheme used for *N*,*N*′-diphenylmalonamide. For *N*,*N*′-dipropylmalonamide the propyl residues were named CA_1, CB_1, CC_1 and CA_2, CB_2, CC_2.

Aniline reacts quantitatively with carbon suboxide, and the product formed precipitates as colorless crystals. The *N*,*N*′-diphenylmalonamide was recrystallized from methanol. Mp: 225–227 °C. ^{1}H-NMR (200 MHz, DMSO): δ 3.48 (H, s, $-CH_2-$), 7.07 (1H, t, phenyl protons para), 7.30 (2H, t, phenyl protons meta), 7.61 (2H, d, phenyl protons ortho), 10.18 (2H, s, –NH–). ^{13}C-NMR (200 MHz, DMSO): δ 46.38 ($-CH_2-$), 119.48 (C_2 phenyl carbon), 123.81 (C_4 phenyl carbon), 129.20 (C_3 phenyl carbon), 139.39 (C_1 phenyl carbon), 165.86 (–CO– amide). The purity of *N*,*N*′-diphenylmalonamide was determined by HPLC: column, RP-18 Spherisorb ODS-2 25 × 0.4 cm; particle size, 5 μm; UV, λ = 254 nm; flow rate = 1 mL/min, eluent, 50% water + 50% acetonitrile. Sample concentration: 1 mg/mL; 20 μl was injected. Only one compound was detected at t_r = 4.82 min (purity = 99.9%).

Synthesis of *N*,*N*′-Dipropylmalonamide. This compound was obtained in a similar way from the reaction of 1-propylamine and carbon suboxide. The *N*,*N*′-dipropylmalonamide was recrystallized from ethyl acetate. Mp: 138–140 °C. ^{1}H-NMR (200 MHz, $CDCl_3$): δ 0.92 (3H, t, $-CH_3$), 1.54 (2H, sext, $-CH_2CH_2N-$), 3.20 (2H, s, $-CH_2-$ malonic), 3.21 (2H, m, $-CH_2CH_2N-$), 7.41 (1H, m, –NH–). ^{13}C-NMR (200 MHz, $CDCl_3$): δ 11.39 ($-CH_3$), 22.54 ($-CH_2CH_2N-$), 41.34 ($-CH_2CH_2N-$), 43.12 ($-CH_2-$ malonic), 167.82 (–CO– amide).

X-ray Diffraction. *N*,*N*′-Diphenylmalonamide. Monocrystals suitable for X-ray diffraction were obtained from a chloroform solution which was slowly evaporated. X-ray data were collected at room temperature using an Enraf-Nonius CAD-4 diffractometer with Mo Kα radiation and a graphite monochromator ($2\theta < 60°$, $\omega - {}^5/_3\theta$ scanning mode). Reflection 107 was measured every hour as an intensity control. No decay was observed. Intensity data were corrected for Lorentz and polarization effects, and absorption was disregarded. Cell dimensions are indicated in Table I, together with other experimental parameters.

The structure was solved by direct methods using the SHELXS-86 computer program package[13] and refined by a full-matrix least-squares procedure.[14] *E*-map revealed all the non-hydrogen atoms, and all the hydrogen atoms in the structure appeared in difference Fourier density maps after 7 cycles of an isotropical and then anisotropical refinement of the non-hydrogen

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Table I. Crystallographic Data

	N,N'-diphenylmalonamide	*N,N'*-dipropylmalonamide
mol formula	$C_{15}H_{14}N_2O_2$	$C_9H_{18}N_2O_2$
cryst size (mm³)	1.1 × 0.3 × 0.1	0.2 × 0.2 × 0.1
cryst syst	orthorhombic	monoclinic
space group	$Pna2_1$	$C2/c$
cell		
a (Å)	9.563 (3)	8.608 (3)
b (Å)	28.135(5)	4.756 (2)
c (Å)	4.919 (2)	28.42 (1)
β (deg)		90.59 (7)
V (Å³)	1323 (1)	1163 (2)
Z (molecules/unit cell)	4	4
asymmetric unit (molecule)	1	1/2
calcd density (g/cm³)	1.276	1.068
radiation (Å)	λ = 0.710 69 (Mo Kα)	λ = 1.541 78 (Cu Kα)
collected reflcns	2283 ($2\theta < 60°$)	2081 ($2\theta < 137°$)
no. of refined param	185	60
$R(\text{int}) = \sum\|F^2 - (F)_{\text{mean}}^2\|/\sum F^2$		0.019
$R(\sigma) = \sum\sigma(F^2)/\sum F^2$	0.028	0.043
unique reflcns	1030 [$I > 2.5\sigma(I)$], $2\theta < 50°$	452 [$I > 3\sigma(I)$]
R factor	0.052	0.084

atoms. The hydrogen atoms bonded to the N atoms were placed in the positions found in the difference Fourier map; the remaining hydrogen atoms were included at calculated positions. All the hydrogen atoms were refined with geometrical constraints ("ride model"). Anisotropic full-matrix refinement for non-hydrogen atoms and isotropic for hydrogens converged to a standard agreement factor $R = 0.052$ for 1024 reflections with $I \geq 2.5\sigma(I)$ and $2\theta < 50°$. We restricted our data to $2\theta_{max} = 50°$ (resolution 0.84 Å), since most structures are limited to this resolution when Cu Kα radiation is used. The R factor increased up to $R = 0.073$ when we used the reflections present up to $2\theta = 60°$ (resolution 0.71 Å). The maximum and minimum heights in the final difference Fourier map were +0.14 and −0.15 e Å⁻³, respectively. A micro-Vax 2000 computer was used for all the calculations.

***N,N'*-Dipropylmalonamide.** Crystals suitable for X-ray diffraction were obtained by slowly cooling a warm ethyl acetate solution (60 °C). X-ray data were collected at room temperature using an Enraf-Nonius CAD-4 diffractometer with Cu Kα radiation and a graphite monochromator ($2\theta < 137°$, ω scanning mode). Data collection was carried out in the triclinic system with cell dimensions $a = 4.756$ (2), $b = 4.905$ (3), $c = 28.35$ (1) Å; $\alpha = 90.51$ (7), $\beta = 89.95$ (4), $\gamma = 118.91$ (7)°. Three reflections were measured every hour as an intensity control. The total exposure time was 16.1 h. The total loss in intensity in that time was 0.8%. Intensity data were corrected for Lorentz, polarization, and decay effects, and absorption was disregarded. The actual crystal system and space group were defined after data reduction and structure solution in different triclinic and monoclinic space groups. The resulting space group and cell dimensions are indicated in Table I, together with other experimental parameters.

The structure was solved by direct methods as described above for *N,N'*-diphenylmalonamide. The hydrogen atoms bonded to the C_2 and N_1 atoms were placed in the positions found in the difference Fourier map. The remaining hydrogen atoms were included at calculated positions. Bond length constraints were also applied to the CA_1–CB_1 and CB_1–CC_1 bonds. The final R factor was 0.084 for 452 reflections with $I > 3.0\sigma(*I)$. The maximum and minimum heights in the final difference Fourier map were +0.21 and −0.18 e Å⁻³, respectively. A micro-Vax 2000 computer was used for all the calculations.

Results

General Features of Malonamide Conformation. A scheme of a malonamide residue is given in Figure 1. In an all-trans conformation the two oxygens of malonamide are close in space. Furthermore, the dipole moments of the two peptide groups are in a parallel, unfavorable orientation. These unfavorable features are removed by rotation around the methylene–carbonyl bonds (ψ angles).

Table II. Fractional Atomic Coordinates with Estimated Standard Deviations in Parentheses and Equivalent Isotropic Thermal Parameters (Å²) for *N,N'*-Diphenylmalonamide

	X/A	*Y/B*	*Z/C*	BEQ
N_1	0.7604 (4)	−0.2755 (1)	−0.136 (1)	3.8
C_1	0.6704 (4)	−0.2479 (2)	−0.008 (1)	3.9
O_1	0.5437 (3)	−0.2491 (1)	−0.041 (1)	5.9
C_3	0.7333 (5)	−0.2135 (2)	0.198 (0)[a]	4.0
C_2	0.7249 (6)	−0.1637 (2)	0.091 (1)	4.2
O_2	0.7272 (5)	−0.1549 (1)	−0.156 (1)	6.4
N_2	0.7197 (4)	−0.1293 (1)	0.282 (1)	4.0
CA_1	0.7350 (4)	−0.3107 (2)	−0.338 (1)	3.6
C_4	0.6045 (5)	−0.3278 (2)	−0.400 (2)	5.0
C_5	0.5913 (6)	−0.3626 (2)	−0.600 (2)	6.1
C_6	0.7041 (6)	−0.3800 (2)	−0.737 (2)	5.7
C_7	0.8339 (6)	−0.3632 (2)	−0.673 (2)	5.5
C_8	0.8502 (5)	−0.3285 (2)	−0.476 (2)	4.7
CA_2	0.7262 (5)	−0.0795 (2)	0.241 (1)	4.2
$C_{8'}$	0.8156 (6)	−0.594 (2)	0.046 (2)	5.9
$C_{7'}$	0.8228 (8)	−0.0101 (2)	0.025 (2)	7.1
$C_{6'}$	0.7422 (9)	0.0182 (2)	0.193 (2)	7.8
$C_{5'}$	0.6555 (8)	−0.0021 (2)	0.382 (2)	7.2
$C_{4'}$	0.6461 (6)	−0.0511 (2)	0.405 (2)	5.4
H_1	0.8542 (4)	−0.2725 (1)	−0.091 (1)	4.0
H_2	0.7147 (4)	−0.1401 (1)	0.451 (1)	7.8

[a] Z-coordinate of the C_3 atom was fixed during refinement.

Table III. Selected Torsion Angles (deg) for *N,N'*-Malonamide Derivatives[a]

					phenyl	propyl
CB_1/C_8	CA_1	N_1	C_1	(φ_1)	168.4	−114.9
CA_1	N_1	C_1	C_3	(ω_1)	180.0	−175.7
N_1	C_1	C_3	C_2	(ψ_1)	108.5	114.8
C_1	C_3	C_2	N_2	(ψ_2)	153.1	114.8
C_3	C_2	N_2	CA_2	(ω_2)	172.8	−175.7
C_2	N_2	CA_2	$CB_2/C_{4'}$	(φ_2)	143.4	−114.9

[a] Note: The molecules present in the crystal and related by glide plane symmetry have the same torsion angles, but with all signs changed.

Depending on ψ, the relative orientation of the two peptide groups will vary. Inter- or intramolecular hydrogen bonds may form depending on the chemical nature of the substituents which are attached to the malonamide unit, as will be shown.

Structure of *N,N'*-Diphenylmalonamide. A scheme of the molecule is shown in Figure 1, and the main X-ray diffraction results are given in Table I. The unit cell contains four equivalent molecules, two of which are mirror images of the other two. Atomic coordinates and torsion angles are given in Tables II and III. Bond lengths and angles are given as supplementary material. In spite of the chemical symmetry of this molecule, its identical halves show different conformational angles. In a symmetric conformation we would expect a diad axis or mirror plane placed on the central CH_2 group, so that both peptide groups should rotate equal amounts ($\psi_1 = \psi_2$). In this case ψ_1 and ψ_2 have different values (108.5° and 153.1°), as shown in Table III. This behavior is found in most malonamide derivatives (for comparison, see Table V). A stereopair with a single molecule is presented in Figure 2, where the lack of symmetry of the molecule is obvious.

The main stereochemical feature of this molecule is that an all-trans conformation ($\psi_1 = \psi_2 = 180°$) is not allowed because the carbonyl oxygens are then very close and at the same time the peptide dipoles are in an unfavorable parallel orientation. Thus the two peptide groups rotate away from each other, but, instead of doing so by equal amounts, in this case they rotate 108.5° and 153.1°. This orientation of the peptide groups generates two perpendicular infinite systems of hydrogen-bonded peptide

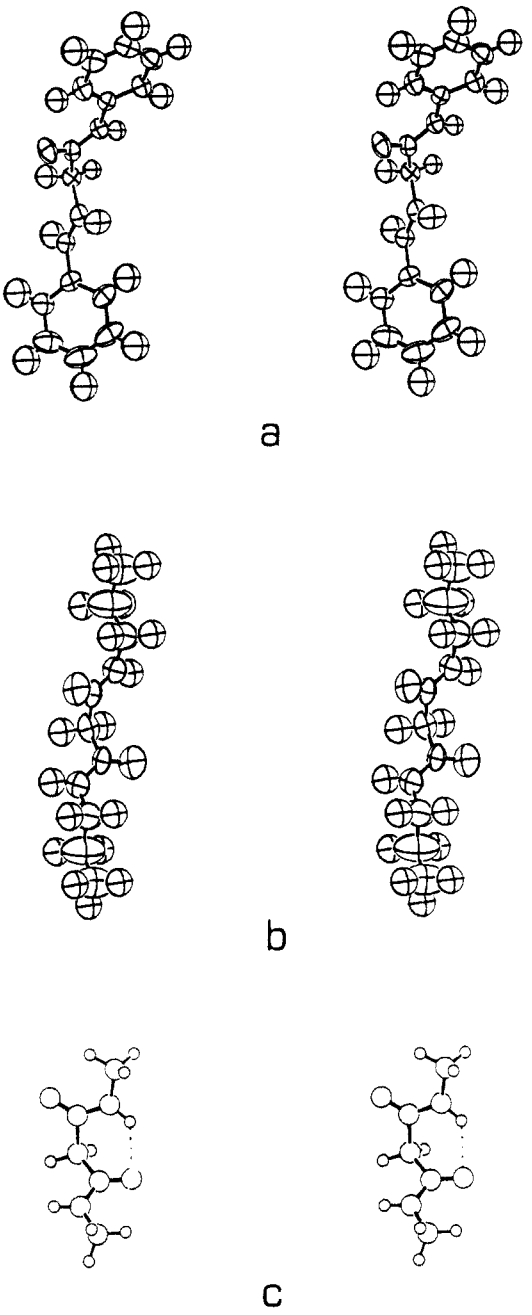

Figure 2. Stereopairs showing the conformation in the crystalline state of *N,N'*-diphenylmalonamide (a) and *N,N'*-dipropylmalonamide (b). The atoms are indicated with their thermal ellipsoids. A hypothetical conformation for *N,N'*-dimethylmalonamide with an intramolecular hydrogen bond (dotted line) is also shown (c).

groups along the *a* and *c* directions of the crystal, as shown in Figures 3 and 4.

The phenyl groups are oriented so that the aromatic rings pile up in the crystal as shown in Figure 3. One ring is almost parallel to the peptide plane (angle 169°), whereas the other ring forms an angle of about 139° with the corresponding peptide plane.

Structure of *N,N'*-Dipropylmalonamide. Atomic coordinates and torsion angles are given in Tables III and IV. A stereoview of the molecule is shown in Figure 2. In this case the crystal has a diad axis on the central methylene group of the molecule, so that it is symmetric and the two torsion angles ψ_1 and ψ_2 are identical. The unit cell contains four molecules, two of which are identical and have the parameters given in Tables III and IV. The other two molecules are related by glide plane symmetry and are their mirror images.

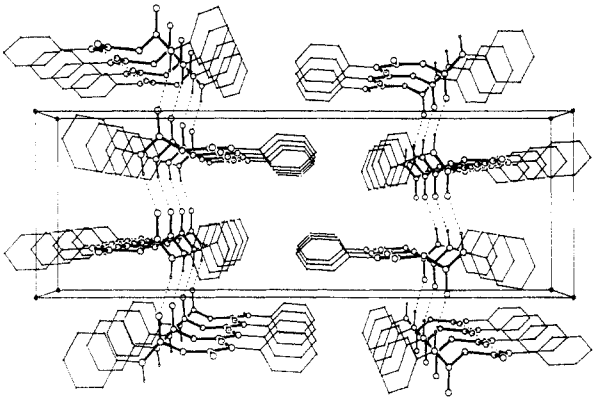

Figure 3. Crystal packing of *N,N'*-diphenylmalonamide viewed down the *c* axis. The *b* axis is horizontal in the figure. Only the amide hydrogens are indicated. The $O_1\cdots H_1$ hydrogen bond system is parallel to the *a* axis and the $O_2\cdots H_2$ to the *c* axis.

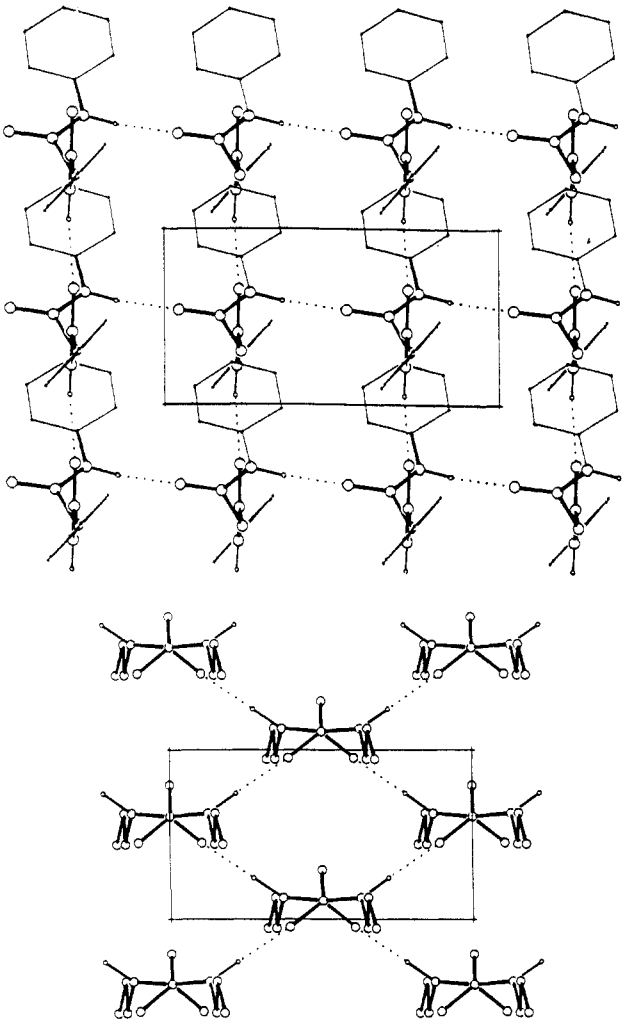

Figure 4. Organization of hydrogen bonds in crystals of malonamide derivatives. They are usually organized in continuous rows which form an overall angle of 90° or 120°, as indicated in Table V. In the figure are shown the projections of one layer of molecules onto the *ac* plane for *N,N'*-diphenylmalonamide (upper figure) and the *ab* plane for *N,N'*-dipropylmalonamide (lower figure). The arrows indicate the overall direction of hydrogen bonds.

A view of the unit cell is shown in Figure 4. Each molecule is associated through hydrogen bonds with four neighboring molecules, so that two directions of hydrogen bonding forming an angle of about 120° are present in the crystal. As we will show in a forthcoming publication, such organization is also found in *n*,3 nylons. The organization of the molecules is pseudohexagonal, since

Table IV. Fractional Atomic Coordinates with Estimated Standard Deviations in Parentheses and Equivalent Isotropic Thermal Parameters (Å²) for *N,N'*-Dipropylmalonamide

	X/A	Y/B	Z/C	BEQ
C3[a]	0.5000(0)	0.291 (2)	0.2500 (0)	6.6
C_1	0.5013(6)	0.110 (1)	0.2933 (2)	5.7
O_1	0.3937(5)	−0.046 (1)	0.3023 (2)	9.1
N_1	0.6273(5)	0.127 (1)	0.3196 (2)	6.8
CA_1	0.6496(9)	−0.053 (2)	0.3613 (3)	10.2
CB_1	0.653(1)	0.128 (2)	0.4048 (3)	15.4
CC_1	0.678(1)	−0.055 (2)	0.4476 (3)	17.4
H_1	0.7215(5)	0.243 (1)	0.3119 (2)	8.7
H_3	0.4015(0)	0.430 (2)	0.2498 (0)	8.7

[a] The C_3 atom is at a special position on the rotation diad $x = 1/2$, y, $z = 1/4$. The atomic coordinates of the other half-molecule are obtained by the symmetry operation $1 - x$, y, $1/2 - z$.

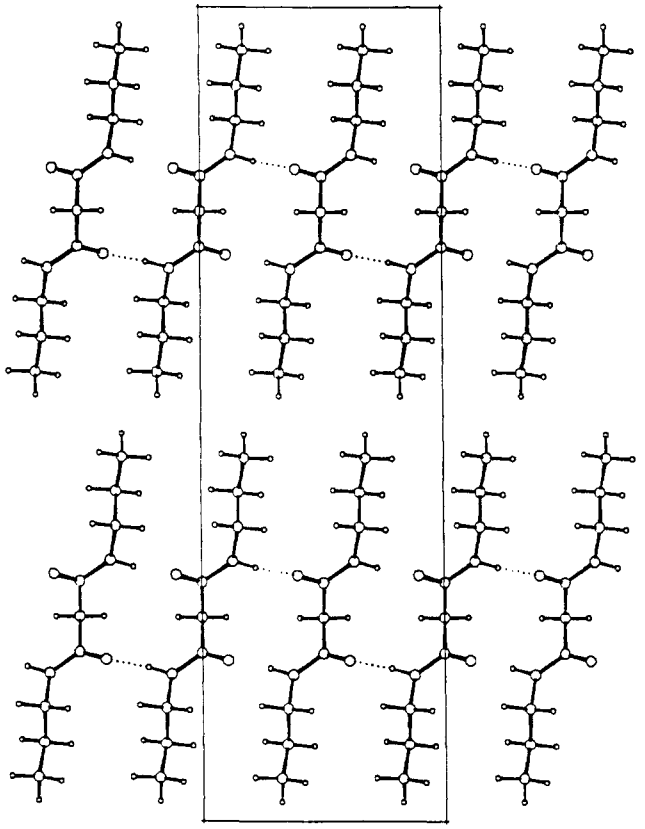

Figure 5. Projection of the crystalline structure of *N,N'*-dipropylmalonamide onto the *ac* plane. Neighbor molecules are at different levels in the *b* direction.

the distance between a molecule and its hydrogen-bonded neighbors is 4.92 Å, whereas the distance to the other two closest molecules (along the *b* axis) is practically identical, 4.76 Å. The angles of the vectors between neighboring molecules are all close to 60°.

A projection parallel to the direction of the propyl chains is shown in Figure 5. The crystal is organized with fully extended parallel, propyl chains, in a similar way to what is found in *n*,3 nylons. The propyl chains have a rather large degree of thermal disorder, as shown in Figure 2, since they are only loosely packed at the surface of interaction among the terminal methyl groups.

Comparison with Other *N,N'*-Malonamide Derivatives. As stated in the Introduction, the structures of a few other *N,N'*-malonamide derivatives are known. All of them have additional hydrogen-bonding groups which create a complex packing network. However, the conformation of the central malonamide group is rather similar to the conformation of the compounds we have described here, as is clearly apparent from Table V. Most of the ψ_1, ψ_2 angles are in the 100–150° range, also found in the compounds studied by us. Depending on the crystal system, packing usually occurs in one of the two ways represented in Figure 4, with two directions of hydrogen bonding either at 90° or 120°. In those cases where other hydrogen-bonding or ionic interactions are available, hydrogen bonds may form with other groups present in the crystal and the hydrogen-bonding network becomes discontinuous and more complicated, as is the case of DUDCEK01 and FUZYUU in Table V. It should be noted that in no case is an intramolecular hydrogen bond such as the one shown in Figure 2c present.

Table V. Conformational Angles of Malonamide Derivatives ($RNHCOCH_2CONHR'$) in Crystals[a]

R, R'	ψ_1	ψ_2	H-bond direction (angle)[b]	ref[4]
C_6H_5	108.5	153.1	2 (90°)	this work
$(CH_2)_2CH_3$	114.8	114.8	2 (120°)	this work
H	111.5, 114.8	140.7, 137.7	2 (90°)	MALOAM[c]
OH	108.8	135	1	FUZYUU
NH_2	99	176	2 (90°)	MALDHZ
NH_2, Cl_2Mn	100.7	101.8	none	DUDCEK01
CH_3, $CH_2CONHCH_3$	104.8	111.5	2 (120°)	VEGXUA
$tBuCONHCH(CH_3)$, $CH(CH_3)_2$	125.2	150.2	2 (90°)	Gómez et al.[6]

[a] In most cases the unit cell also contains mirror image molecules with identical but negative angles. [b] There are either one, two, or no continuous hydrogen-bond systems throughout the crystal. The *overall* angle between the H-bond directions is given in the table. The *local* angle between contiguous hydrogen-bonded peptide groups may differ, as is apparent in Figure 4. [c] The crystals of malonamide contain two molecules with slightly different conformational angles.

A striking feature of the results shown in Table V is that the ψ_1 and ψ_2 angles are usually different, while the malonamide residue is chemically symmetric. This is apparently due to an optimization of the packing and hydrogen-bonding interactions found in the crystal. Only seldom does the central methylene group correspond to an element of symmetry of the crystal. In this sense it is interesting to compare the structure of malonodihydrazide (MALDHZ) with that of its $MnCl_2$ adduct. In the first case a complex network of hydrogen bonds is formed and as a result the ψ_1 and ψ_2 angles are particularly different. When the molecule crystallizes in the presence of $MnCl_2$, the interactions of the peptide groups with the ions are not so stringent and the ψ_1 and ψ_2 values became approximately equal and closer to the average value of most compounds.

Comparison with Malonamide Derivatives with Additional Substituents. The conformational behavior of the malonamide unit changes when it has substituents in the central carbon atom. In some cases, where a single substituent is present, the molecules are symmetric, $\psi_1 = -\psi_2$, as shown by Marraud and co-workers in different compounds.[7] A single hydrogen-bonding direction appears involving both peptide groups in each malonamide unit, which are then oriented in parallel. An approximate value of 110° for $\psi_1 = -\psi_2$ gives a structure reminiscent of a β-pleated sheet.

When both methylene hydrogens of the malonamide unit are substituted, the conformation described in the previous paragraph is not possible. Then a six-membered hydrogen-bonded ring is found, similar to that shown in Figure 2c. The values of the ψ_1 and ψ_2 angles are then significantly different from those shown in Table V. For example, the compounds studied by Kálmán et al.[15] and

by Gieren and Dederer[16] have ψ_1/ψ_2 values of 35°/92° and 30°/152°, respectively.

Discussion

Conformation of the Malonamide Residue. Our results and those summarized in Table V show that standard malonamide residues, with at most one substituent in each amino group, have a characteristic conformation with both ψ angles in the range 100–140°, with a few exceptions in which one of the two ψ angles may be larger, as shown in Table V. In spite of the chemical symmetry of many malonamide derivatives, in general, the two angles are not identical due to the packing constraints. The survey we have carried out also indicates that the preferred conformation does not have a sharply defined minimum, since ψ angles between 99° and 176° are found. In most cases the planes of the two peptide groups are approximately perpendicular.

The situation changes when there are substituents in the central methylene carbon. Then a symmetric conformation ($\psi_1 = -\psi_2$) has been found[7] in compounds with a single substituent in the central methylene group. A six-membered hydrogen-bonded system is formed[15,16] when both hydrogens are substituted by bulky substituents. It is striking to note that the latter conformation has been predicted[9-11] to be most stable for simple malonamide derivatives, but in fact it has only been found when the malonamide system is constrained by having two substituents in the methylene group. Dado et al.[5] also noted that the theoretical prediction was not validated in some triamides which form more complicated hydrogen-bonded systems.

Packing Constraints as Related to *n*,3 Polyamides. The diverging orientation of the two peptide groups, best seen in parts a and b of Figure 2, generates two hydrogen-bonding directions which give rise to the packing organization shown in Figures 3–5. If *N,N'*-dipropylmalonamide is an adequate model for polyamides of the nylon *n*,3 type, we should then expect for such polymers a pseudohexagonal organization as that shown in Figures 4b and 5. Such an organization has indeed been found in some of the *n*,3 polyamides. However, these polyamides also show a polymorphism which indicates that other conformations may be possible in the polymer. In fact, Paiaro et al.[1] suggested a conformation in which $\psi_1 = \psi_2 = 60°$ which results in a single direction of hydrogen bonding. A single direction of hydrogen bonding can also be obtained with the angles found by Marraud and coworkers[7] in the methylene-substituted malonamide derivatives. In the conformation suggested by Paiaro et al.[1] the peptide groups are oriented in opposite directions, whereas in the structures found by Marraud and coworkers[7] they point in the same direction. The latter conformation, when placed in the polymer, coincides with the γ form of nylons.[17]

In summary, it appears that *n*,3 nylons should prefer a conformation with two directions of hydrogen bonding at 120°, as has been found in *N,N'*-dipropylmalonamide and which is consistent with the results presently available for *n*,3 nylons.[2,18] However, in view of the polymorphism of this family of polyamides, it cannot be excluded that a conformation with a single hydrogen-bonding direction may also be present in some cases. This question will be discussed in more detail in a forthcoming publication, where additional data on *n*,3 nylons will be reported.

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Supplementary Material Available: Crystallographic details, including Tables 6–13 of anisotropic thermal parameters, bond lengths and angles, hydrogen bond geometries, and complete torsion angles, for *N,N'*-diphenylmalonamide and *N,N'*-dipropylmalonamide (8 pages). Ordering information is given on any current masthead page.

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