A Nonresonated Orthogonally Twisted Amide

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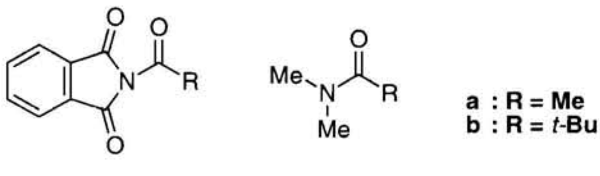
The structure of *N*-pivaloylphthalimide was studied by IR, ^{13}C NMR and UV spectroscopies, and X-ray analysis. The C(O)-N bond is orthogonally twisted, and the bond length is as long as that of C-N single bond.

Planarity of amide groups plays important roles not only in the construction of the high-order structure of enzymes and proteins but also in the physical and chemical properties of various organic molecules, because it provides rigid units and stable bonds. However, it has been known that some peptides, proteins, enzymes[1] and bridgehead lactams[2] have non-planar deformation in the amide moiety. This unusual structure is of interest in relation to the chemical reactivity[3,4] and biochemical functions.[5]

In the course of our studies on the structure and reactivity of twisted amides,[4,6] we were interested in the structure of *N*-acylphthalimides, because the geometries of the amide group have not yet been elucidated,[7] though they have simple structures containing a symmetrical phthalimide framework. In this communication we report that the amide bond of **1b** is orthogonally twisted and the C(O)-N double bond character mostly disappears.

N-Acylphthalimides (**1a**[8] and **1b**[9]) were readily prepared by the reaction of phthalimide with the corresponding acyl chlorides in the presence of Et_3N and DMAP. Both compounds are stable in an open atmosphere for a few months.



1 **2**

Table 1 shows the IR, ^{13}C NMR and UV spectral data of **1a** and **1b**. The data of the acyl carbonyl absorption band of **1a** and **1b** were corrected by subtracting those of the corresponding *N,N*-dimethyl carboxyamides (**2a** and **2b**) to cancel out the substituent effect on the carbonyl group, and the differences were indicated as $\Delta\nu_{C=O}$. The $\Delta\nu_{C=O}$ value of **1b** is much larger than that of **1a**. A similar tendency is also seen in the ^{13}C NMR chemical shifts of carbonyl carbons; among the four carbonyl signals of **1a** and **1b**, only that of the pivaloyl carbonyl carbon of **1b** appears in much lower field. $\Delta\delta$(^{13}C=O) values were also determined by similar way to the $\Delta\nu_{C=O}$ for comparison without the substituent effect. The large difference is still observed between them. The λ_{max} of **1a** is a little longer than that of *N*-methyl phthalimide (217.6 nm), whereas the λ_{max} of **1b** is close to it. These observations suggest that the geometries of **1a** and **1b** are very different each other.

The X-ray crystallographic analysis of **1b** was performed to elucidate its structural details.[10] Figures 1 and 2 give the ORTEP drawing and projection of the amide group down the C-N bond, respectively. There was a significant disorder in the *t*-Bu group due to the rotation about the C-C(CH_3)$_3$ bond. Therefore, the analysis was achieved by dividing each methyl group into three parts. The most significant feature is the orthogonally twisted conformation of the amide group. The twist angle τ[11] is 83.2° (Table 2), which is the highest value ever reported for amides. AM1[12] calculations also support the highly twisted structure. In contrast, the τ value of **1a** is very small, which means the acetyl and phthalimide groups of **1a** to be coplanar. Therefore, the large twist angle of **1b** should be ascribed to the steric repulsion between the imide carbonyl and *t*-Bu groups.[13] The spectral data

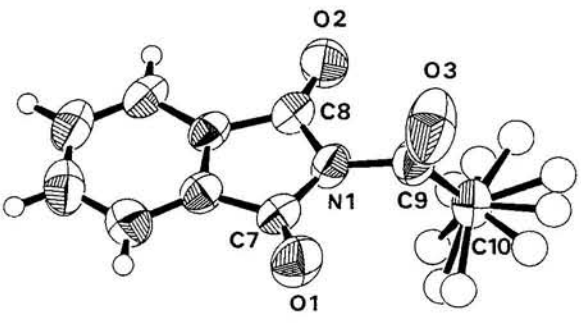


Figure 1. ORTEP drawing of **1b**. Thermal ellipsoids scaled at 50% probability level. The methyl carbons of the *t*-Bu group were described with the small and same size of circles to clarify the disordered structure.

Table 1. IR and ^{13}C NMR spectral data of **1** and **2**, and UV spectral data of **1**

Compd	$\nu_{C=O}$/cm^{-1} ^{a}	$\Delta\nu_{C=O}$/cm^{-1}	λ_{max}/nm^{b}	ε	δ(^{13}C=O)^{c,e}	δ(^{13}C=O)^{d,e}	Δδ(^{13}C=O)^{c}
1a (**2a**)	1714.8 (1634.6)^{f}	80.2	222.4	83300	165.4	168.8 (170.6)^{f}	-1.8
1b (**2b**)	1718.4 (1610.6)^{f}	107.8	218.6	79400	166.1	182.0 (177.5)^{f}	4.5

^{a} In $CHCl_3$. ^{b} In CH_3CN. ^{c} Imide carbonyl. ^{d} Amide carbonyl. ^{e} Recorded at 100.4 MHz in $CDCl_3$. Chemical shifts (ppm) are referenced to internal tetramethylsilane. ^{f} The data of compound **2**.

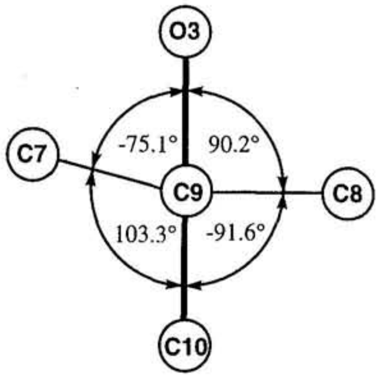


Figure 2. Projection of the amide group of **1b**, down the C-N bond.

Table 2. Dunitz parameters[a] for **1a** and **1b**

Compd	Origin	τ / °	χ_C / °	χ_N / °
1a	AM1	0.1	0.1	0.4
1b	X-ray	83.2	1.6	14.9
1b	AM1	70.4	2.6	16.8

[a] Reference 11.

described above consist the geometrical difference between **1a** and **1b**.

The observed and calculated pyramidalization factor χ_N for **1b** is a little larger than the calculated χ_N for **1a** (Table 2). It has been known that rotation of the C(O)-N bond in amides generally accompanics *N*-pyramidalization, because the hybridization of amide nitrogen changes from sp^2 to sp^3 during the rotation.[2a,14] Since the χ_N value for a sp^3 nitrogen is 60°, it is interesting that the χ_N of **1b** is very small despite the large τ value. This may be attributed to the preserved amide resonance in the phthalimide moiety. Thus, even if the acyl group twists, the lone pair electron of the N atom still can resonate with the imide carbonyl groups, and therefore, the N atom retains sp^2 hybridization.

Table 3. Selected bond lengths of **1b**

Bond	r(C-N)/Å	Bond	r(C=O)/Å
C7-N	1.405(4)	C7=O	1.200(4)
C8-N	1.389(4)	C8=O	1.211(4)
C9-N	1.474(4)	C9=O	1.191(5)

Table 3 gives the observed C-N and C=O bond lengths of **1b**. Remarkable is the length of C9-N of 1.474(4) Å, which is much longer than those of C7-N and C8-N, and is very close to the typical $C(sp^2)$-$N(sp^3)$ bond distance of 1.44 Å,[14] despite small pyramidalization of the N atom. This observation indicates that the C-N double bond character mostly disappears. The shorter C9=O distance than those of C7=O and C8=O also supports the nonresonated amide bond.

In summary, it was found that the conformation of amide moiety changes dramatically depending on the *N*-acyl substituent groups. Steric repulsion between the imide carbonyl and *t*-Bu groups of **1b** causes rotation about the C(O)-N bond at the sacrifice of the resonance stability, and provides an orthogonally twisted amide linkage. The length of the C(O)-N bond is very close to that of general C-N single-bond, though the N atom retains sp^2 hybridization. From these observations it is concluded that the amide resonance in **1b** is mostly lost.

References and Notes

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10 Crystal data for **1b** : $C_{13}H_{13}NO_3$, M = 231.24, monoclinic, space group $P2_1/c$, a = 11.6720(3), b = 6.939(3), c = 15.6877(1) Å, V = 1215.2(5) $Å^3$, Z = 4, ρ_{calcd} = 1.264 Mgm^{-3}, m = 0.745 mm^{-1}(Cu-$K\alpha$, λ = 1.54178 Å), $F(000)$ = 488, T = 293 K. A total of 1898 unique data for 2Θmax = 120° was collected of which 1800 were independent. Structure was solved by direct methods with SHELXS-86 (G. M. Sheldrick, Program for the solution of crystal structures, 1986, University of Gottingen, Germany) and refined on F^2 using the SHELXL-93 (G. M. Sheldrick, Program for the refinement of crystal structures, 1993, University of Gottingen, Germany). Non-hydrogen atoms except for the three methyl carbons of the *t*-Bu group were refined anisotropically by full-matrix least squares method. Each methyl carbons of the *t*-Bu group was divided to three parts, and they were refined with ocupation factors of 0.5, 0.3, and 0.2. The H atoms except for methyl hydrogens were treated isotropic. The R and Rw factors after refinement of 164 parameters using 1610 observed refrections [$I > 2\sigma(I)$] were 0.0874 and 0.2347, respectively. The max. and min. residual electron densities were 0.409 and -0.388 $eÅ^{-3}$, respectively. CCDC-100651.

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