Photoinduced switching of intramolecular hydrogen bond between amide NH and carboxylic oxygen

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Electrically Supplemental Information

Contents

1. Crystallographic data

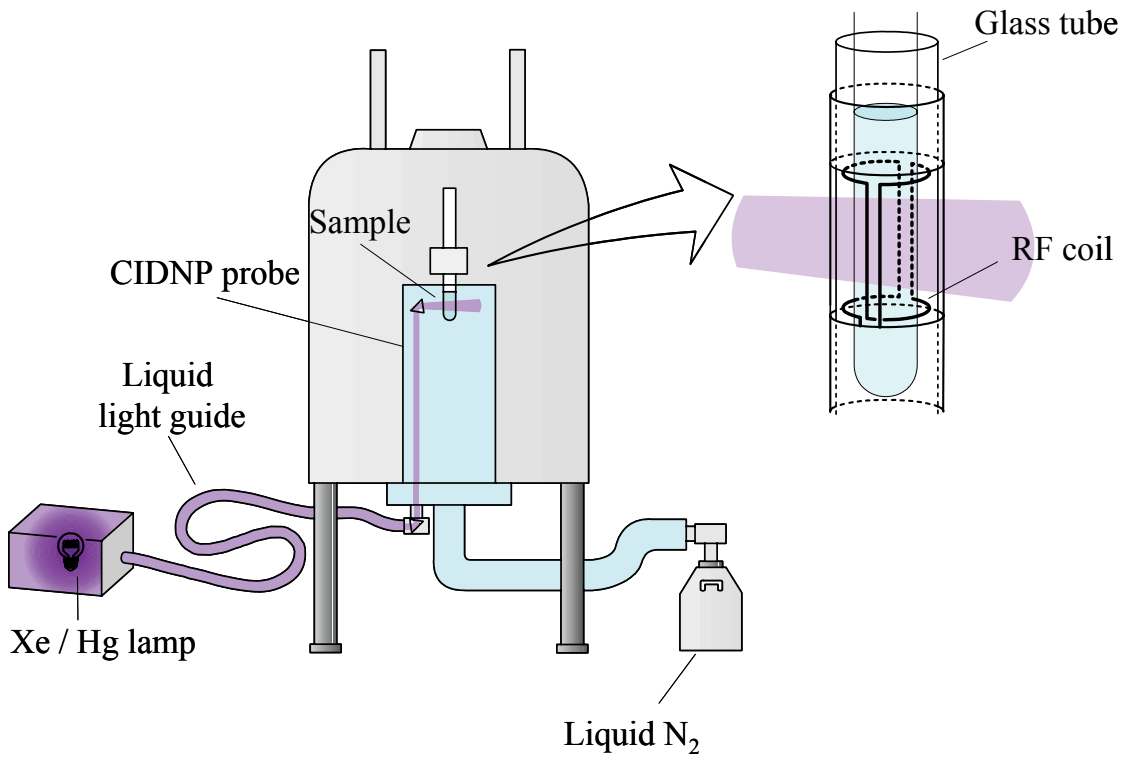
Crystallographic Data Collections and Structure Determinations of tetramethyl -ammonium; (*E*)-3-{[3-(2,2-dimethyl-propionylamino)-benzylidene-amino]-benzoate (*E*-2). A suitable single colorless crystal of tetramethyl-ammonium; 3-{[3-(2,2-dimethyl-propionylamino)-benzylidene-amino]-benzoate (*E*-2) was mounted on a fine nylon loop with nujol and immediately freezed at 200 K. All measurements were performed on a Rigaku RAXIS-RAPID Imaging Plate differactometer with graphite monochromated MoK α radiation. The structures were solved by direct method (SIR 92) and the following refinements were performed using SHELXL-97 and teXsan crystallographic software package. All non-hydrogen atoms were refined anisotropically. H1 was placed by reflection and hydrogen atoms without H1 were placed in the calculated position and including least-square refinement. The basic crystallographic parameters are listed in Table S1.

Table S1. Crystal Data and Collection Parameters

Complex	***E*-2**
Formula	$C_{23}H_{31}N_3O_3$
Formula weight	397.52
Crystal Color, Habit	colorless, platelet
Crystal Dimensions, mm	0.30 X 0.30 X 0.20
Crystal system	monoclinic
Space group	$P2_1/n$
A, Å	16.08(2)
B, Å	8.501(8)
C, Å	17.00(3)
α, deg	—
β, deg	104.5(1)
γ, deg	—
V, Å ^{3}	2249(1)
Z	4
D_{calc}, g/cm^3	1.173
F (000)	1856.00

Radiation	MoKα
Temp, ^{o}C	-73±1
$2\theta_{max}$, deg	54.5
Unique data	21943
Unique data (I>3σ(I))	5009
No. of variables	262
R_1	0.059
$_wR_2$	0.103
GOF	0.86
Max Shift / Error	0.00

2. Schematic illustration of low temperature ^{1}H NMR spectrum measurement



3. COSY NMR spectrum of *E*-2'/*Z*-2' under photoirradiation

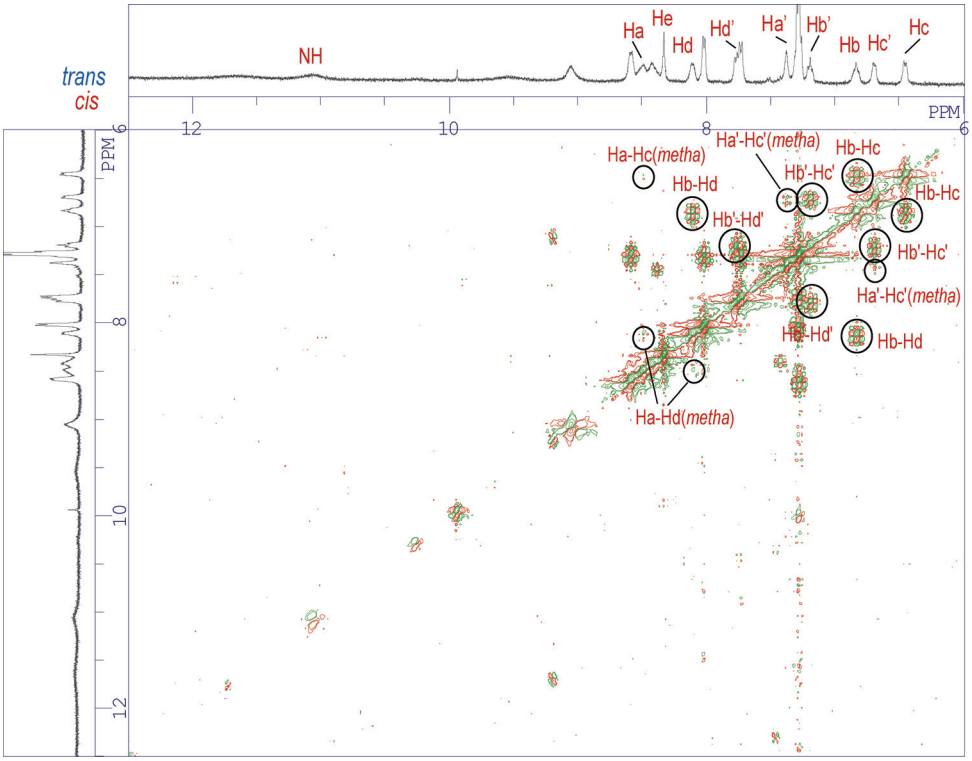


Fig. S1 Photoirradiating COSY NMR spectrum of carboxylate (*E*-2'/*Z*-2') 5 mM in THF-d_8 solution at 203 K.

COSY NMR spectrum was measured under photoirradiation to assign the signals of *Z*-2'. *ortho*-Coupling between Hc-Hb-Hd and Hc'-Hb'-Hd' and *meta*-coupling between Ha-Hc-Hd and Ha'-Hc' were observed.

4. First-order kinetics of thermal isomerization of *Z*-1 and *Z*-2'

Thermal reversion rate constants of carboxylic acid *Z*-1 and carboxylate *Z*-2' in the temperature range from 213 to 243 K were measured by using the time course experiments of UV-vis spectra at 313 nm. Thermal reversion rate k was obtained from the equation (1). The thermal reversion rate constants were obtained from the slopes of the plots, $ln\ [A_{trans} / (A_{trans} - A(t))]$ versus time(t).

$$kt = ln\ [A_{trans} / (A_{trans} - A(t))] \quad (1)$$

A_{trans} : 313 nm optical density of *trans* isomer,

$A(t)$: 313 nm optical density at t seconds after irradiation was finished

The thermal reversion rate constants of *Z*-1 and *Z*-2' at several temperatures were shown in Table S2. The thermal reversion of carboxylic acid *Z*-1 was faster than that of carboxylate *Z*-2' in the region from 213 to 243 K. This result indicates that the NH···O intramolecular hydrogen bond forming at carboxylate *Z*-2' is stronger than that of carboxylic acid *Z*-1.

Activation energies of thermal reversion of *Z*-1 and *Z*-2' were obtained from the equation (2), so called *Arrhenius's plot*.

$$k = A\ EXP(-E / RT) \quad (2)$$

（ R : gas constant, T : absolute temperature, E : activation energy, A : frequency factor ）

Table S2 Thermal Reversion Rates from *Z* to *E* Iisomers

Temp. (K)	*Z*-1 / E-1	*Z*-2' / *E*-2'
243	3.1×10^{-2}	1.3×10^{-2}
233	9.5×10^{-3}	3.4×10^{-3}
223	1.9×10^{-3}	5.6×10^{-4}
213	4.0×10^{-4}	1.0×10^{-4}