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Coerced photodimerization reaction in the solid state through amine salt formation

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Abstract—Photodimerization of fumaric or several γ-form *trans*-cinnamic acids proceeded successfully in the solid state through amine salt formation with ammonia or some aromatic heterocyclic amines (especially, imidazole). It appears that this success is due to a small size or a planar structure of the amine. A layered or a channel-type clathrate crystal structure was revealed, respectively.

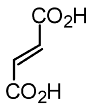
1. Introduction

An intriguing feature on the chemistry of organic crystal is that some of the crystals are reactive and others are unreactive, even though the difference of their molecular structure is minor.[1] The reactivity and selectivity in the solid state is mostly controlled by the crystal structure, but unfortunately it is still difficult to construct a desired one. Therefore, an attempt for developing simple experimental methods to compel photoinert crystals to be reactive will be of significance. In this connection, we and others have been investigating photochemical reactions of two-component crystals.[2,3]

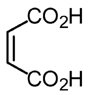
We have already explored orientational control over the solid-state photodimerization of specific compounds like *trans*-cinnamic acids,[4] anthracenecarboxylic acids,[5] and *trans*-cinnamamides[6] by using diamines (for the acid case) or dicarboxylic acids (for the amide case). Diamines and dicarboxylic acids were expected to function as a non-covalent linker, i.e. to connect two monomer molecules in a sort of pre-designed orientation. A problem met there, however, was that many of those hydrogen-bonded co-crystals have little or no reactivity. We felt that the main cause for such a lack of reactivity would be due to the steric bulkiness of the linker. Hence, we have investigated the effect of the amine size on the attempted photodimerization in aminium salts of specific alkenoic acids.[7]

2. Results and discussion

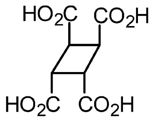
Fumaric acid (**1**) is photostable in the solid state, as we confirmed.[†] In order to change the reactivity of **1**, we prepared many crystalline salts from **1** and alkylamines (**a**–**m**) having a series of alkyl groups (**1**/amine=1:2 or 1:1; Table 1). These crystals were pulverized and were irradiated at 254 nm for 40 h under an argon atmosphere. Our method for the solid-state photolysis was described previously.[2,4–6] After the photolysis, product compositions were estimated by NMR (in DMSO-d_6). The results are summarized in Table 1. It can readily be seen that diammonium fumarate (**1h**), i.e. the salt with the smallest amine, underwent photodimerization to give almost selectively *cis*,*trans*,*cis*-1,2,3,4-cyclobutanetetracarboxylic acid (CBTA). Other salts afforded essentially no CBTA. On the other hand, *trans*,*cis*-photoisomerization leading to maleic acid was achieved relatively easily except **1h** and **1i**. This is interesting because *trans*,*cis*-photoisomerization of an alkene double bond is generally inefficient in the solid state.[1]



fumaric acid
(**1**)



maleic acid



CBTA

We have found that two kinds of the co-crystal of **1** with guanidine hydrochloride $(H_2N)_2C{=}NH{\cdot}HCl$ (**n**) (**1**/**n**=8:1 and 3.7:1 based on the C, H, N, Cl-elemental analysis, mp 229–237 and 208–226°C, respectively) can afford CBTA in a reasonable yield (CBTA 31 and 25%, **1** 66 and 69%, maleic acid 3 and 6%, respectively). This result suggests

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Keywords: solid state; photodimerization; fumaric acid; cinnamic acid; amine salt; imidazole.

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[†] On the other hand, we found that maleic acid, which was recrystallized from wet benzene, photoreacted in the solid state to give quantitatively CBTA: 82% conversion after 100 h irradiation of maleic acid (80 mg) with a low pressure mercury lamp (254 nm) under Ar atmosphere at room temperature.

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Table 1. Product compositions of the solid state photolysis of ammonium fumarates **1a–1m**, prepared from fumaric acid (**1**) and alkylamines **a–m**

Salt	Amine **a–m**	**1**/amine[a]	Product composition (%)			Recovered amine (%)
			CBTA	Fumaric acid (**1**)	Maleic acid	
1a	t-BuNH$_2$	1:2	Trace	50	50	100
1b	(±)-s-BuNH$_2$	1:2	1	35	65	100[b]
1c	(S)-s-BuNH$_2$	1:2	Trace	35	65	100[b]
1d	PrNH$_2$	1:2	0	57	43	97
1e	i-PrNH$_2$	1:2	0	63	37	100
1f	EtNH$_2$	1:2	0	89	11	96
1g	MeNH$_2$	1:2	0	87	13	96
1h	NH$_3$	1:2	84	15	1	ne[c]
1i	PhCH$_2$NH$_2$	1:2	0	98	2	100
1j	(±)-t-chxn	1:1	0	70	30	100
1k	(S,S)-t-chxn	1:1	0	63	37	100
1l	c-chxn	1:1	1	84	15	100
1m	Et$_3$N	1:1	0	89	11	92

Irradiation was carried out for 40 h with a 10 W low-pressure mercury lamp at room temperature.

[a] Molar ratios based on elemental analysis.

[b] The photolysate melted during irradiation. Irradiation at 0°C afforded similar results.

[c] Not estimated.

that besides the smallest amine (ammonia), planar amines may be used in order to dimerize **1**. We therefore prepared many aminium salts from **1** employing aromatic heterocyclic amines **A–I** (**1**/amine=1:1 except **1I** where it is 1:2; Table 2). They were irradiated in the solid state and the results are summarized in Table 2.

Table 2. Product compositions of the solid state photolysis of aminium fumarates **1A–1I**, prepared from fumaric acid (**1**) and aromatic heterocyclic amines **A–I**

Salt	**1**/amine[a]	Product composition (%)			Recovered amine (%)
		CBTA	Fumaric acid (**1**)	Maleic acid	
1A	1:1	89	11	0	100
1B	1:1	27	73	Trace	100
1C	1:1[b]	14	82	0[c]	36[d]
1D	1:1[b]	26	72	2	0[d]
1E	1:1	13	87	0	100
1F	1:1	46	54	0	100
1G	1:1	1	99	0	100
1H	1:1	10	90	Trace	100
1I	1:2	No reaction			100

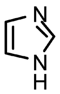
Irradiation was carried out for 40 h with a 10 W low-pressure mercury lamp at room temperature.

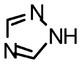
[a] Molar ratios based on elemental analysis, unless otherwise specified.

[b] Based on NMR analysis. The elemental analysis gave a value less than unity for the amine component.

[c] Another product: **2**, 4%.

[d] Lost during the irradiation.


A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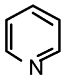
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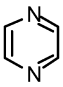
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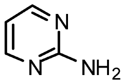
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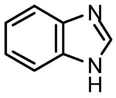
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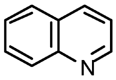
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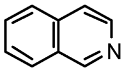
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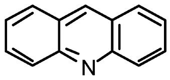
I

Table 2 demonstrates that all of the salts with the aromatic heterocyclic amines, except **1G** and **1I**, produce CBTA with negligible formation of maleic acid. The salt with imidazole (**A**) **1A** gave the best result, producing selectively CBTA in a high yield. In the case of **1C**, betaine **2** was formed as a byproduct, which was decarboxylated into **3** in hot DMSO (see Scheme 1). It is known that fumaric acid (**1**) and some pyridine compounds can react slowly to give betaines, e.g. pyridine (**C**) gave **2** in about 20% yield on heating at 50°C for 50 h in methanol.[8] The reactivities for the pyridine compounds were shown to depend on both their basicity and steric effects.[8] The present experiment suggests that **2** can be formed also by the solid state photolysis, since the crystal **1C** is unreactive in the dark. Comparing the pK_a values for **A**, **C**, **D**, **E**, **F**, **G**, **H**, and **I** (6.95, 5.25, 0.65, 3.45, 5.53, 4.90, 5.42, and 5.58, respectively), the basicity of **C** (pK_a 5.25) is medium and thus it cannot rationalize the characteristic betaine formation observed uniquely in **1C**.

Several substituted *trans*-cinnamic acids, for instance, *o*-methyl- (**4**), *m*-methoxy- (**6**), *p*-methoxy- (**7**) and *m*-chlorocinnamic acid (**8**),[9] are known to take a photoinert γ-crystal modification.[‡] The crystal form of *m*-methylcinnamic acid (**5**) is not reported. We irradiated the crystal of **5** (recrystallized from ether) and found only slow and complex reactions (see the bottom row in Table 3). Hence, the crystal structure of **5** must be unsuitable for photodimerization. Now we prepared ammonium salts **4h–8h** from these cinnamic acids. The ammonium salt **9h** of unsubstituted *trans*-cinnamic acid (**9**) was also prepared for comparison. The most stable crystal modification of **9** is known to be an α-structure and is photochemically converted into α-truxillic acid.[9]

To our surprise, all these salts underwent photodimerization to yield exclusively or mainly head-to-head dimers, i.e. β- and δ-truxinic acids (Table 3). We had previously observed that many of the double salts of *trans*-cinnamic acids with diamines were inert to photodimerization.[4] As a result, ammonia appears to be a very good base to cause

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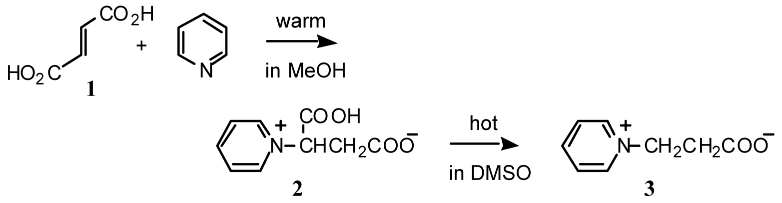
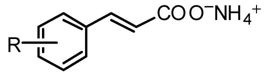
[‡] According to the previous paper, **8** is polymorphic: β or γ.[9] In our hands, however, we always obtained a γ-form. While **7** is photostable in the crystalline state,[9] its photodimerization at the air/solution interface[10] or in vesicles[11] proceeded effectively.



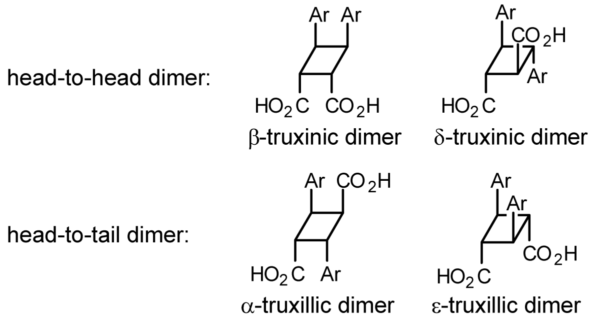
Scheme 1.

photodimerization of fumaric and particular *trans*-cinnamic acids in the solid state.[§]



4h - 9h

R = o-Me (**4h**), m-Me (**5h**), m-OMe (**6h**), p-OMe (**7h**), m-Cl (**8h**), H (**9h**)



We have already reported the crystal structures of diammonium fumarate (**1h**) and bis(isopropylammonium) fumarate (**1e**).[12] For the photodimerizable **1h**, the layer of ammonium ions (NH_4^+) and the layer of fumarate ions ($^-O_2CCH{=}CHCO_2^-$) are alternately arrayed (Fig. 1(A)). Since the size of NH_4^+ is small, the fumarate ions are juxtaposed with good overlap. The intermolecular distance between the C=C double bonds of the fumarate is 3.73 Å, and thus is suitable for the photodimerization.[1,13] The crystal structure of **1e** is also layered (Fig. 1(B)). Here, however, the fumarate layers are far separated from each other, because the C–N bond in the cation (i-$PrNH_3^+$) is directed nearly perpendicular to the layers. Thus, the separation of the pertinent C=C double bonds is longer than 7.2 Å, which corresponds with the lack of photodimerization in **1e**.[¶][1,13]

The X-ray crystal structure of **1A** is shown in Figure 2. There are one molecule of hydrogen fumarate anion ($HO_2CCH{=}CHCO_2^-$) and one molecule of imidazolium cation (imidazoleH$^+$) in the asymmetric unit. Planar imidazolium cations are stacking along the **a** axis, forming a column. Between the columns of the cation, there is a channel, where the planar hydrogen fumarate anions are aligned as guest in pairs with good overlap. The intermolecular distance between the C=C double bonds of the fumarate pair is 3.76 Å. These structural data can well rationalize the efficient photodimerization observed in **1A** (Table 2).

3. Conclusion

In summary, in the successful photodimerization of fumaric acid or several γ-form *trans*-cinnamic acids in the solid state, ammonia (i.e. the smallest amine) and some aromatic heterocyclic amines (especially, imidazole) allowed high yields of the corresponding dimers to be formed through amine salt formation. It appears that a small or a planar complexing agent is a good foreign molecule for converting photostable crystal packing into photodimerizable.

4. Experimental

4.1. General

^1H NMR spectra were measured on a JEOL EX-270J spectrometer. The solvent employed is DMSO-d_6, unless otherwise specified. IR spectra were recorded with a SHIMADZU FTIR-8100A spectrometer (in KBr and/or nujol). Mass spectra were obtained in a JEOL JMS-HX 110A spectrometer. Melting points were measured on a YANACO MP-S3 microscopic hot-stage and are uncorrected.

4.2. Materials

All the starting compounds we employed, i.e. fumaric acid (**1**), *tert*-butylamine (**a**), *sec*-butylamine (**b**), (*S*)-(+)-*sec*-butylamine (**c**), propylamine (**d**), isopropylamine (**e**), ethylamine (**f**), methylamine (**g**) (40% MeOH solution), ammonia (**h**) (28% aqueous solution), benzylamine (**i**), *trans*-1,2-diaminocyclohexane (*t*-chxn, **j**), (1*S*,2*S*)-(+)-*trans*-1,2-diaminocyclohexane ((*S*,*S*)-*t*-chxn, **k**), *cis*-1,2-diaminocyclohexane (*c*-chxn, **l**),

Table 3. Product compositions of the solid state photolysis of ammonium *trans*-cinnamates **4h–9h**

Salt	R	Product composition (%)			
		h–h dimer (β,δ)	h–t dimer (ε)[a]	*Cis*	*Trans*
4h	*o*-Me	47 (13, 34)	0 (0)	18	34
5h	*m*-Me	62 (29, 33)	1 (1)	4	33
6h	*m*-Ome	100 (22, 78)	0 (0)	0	0
7h	*p*-Ome	68 (68, 0)	0 (0)	0	14[b]
8h	*m*-Cl	79 (79, 0)	0 (0)	0	0[b]
9h	H	90 (80, 10)	7 (7)	3	0
5	*m*-Me	4 (4, 0)	0 (0)	Trace	75[b]

Irradiation was carried out for 10 h with a 400 W high-pressure mercury lamp at 10°C.

[a] The α isomer was undetectable in all cases.

[b] Polymeric materials were also formed.

[§] However, we could not obtain a crystalline ammonium salt from caffeic or ferulic acid.

[¶] The crystal structure of **1m** was also reported.[14] It was assigned as triethylammonium hydrogen fumarate ($HO_2CCH{=}CHCO_2^-$)(Et_3NH^+). Fumarate double bonds are nonparallel and more than 4.5 Å away, which explains[1,13] the absence of CBTA from **1m** (Table 1).

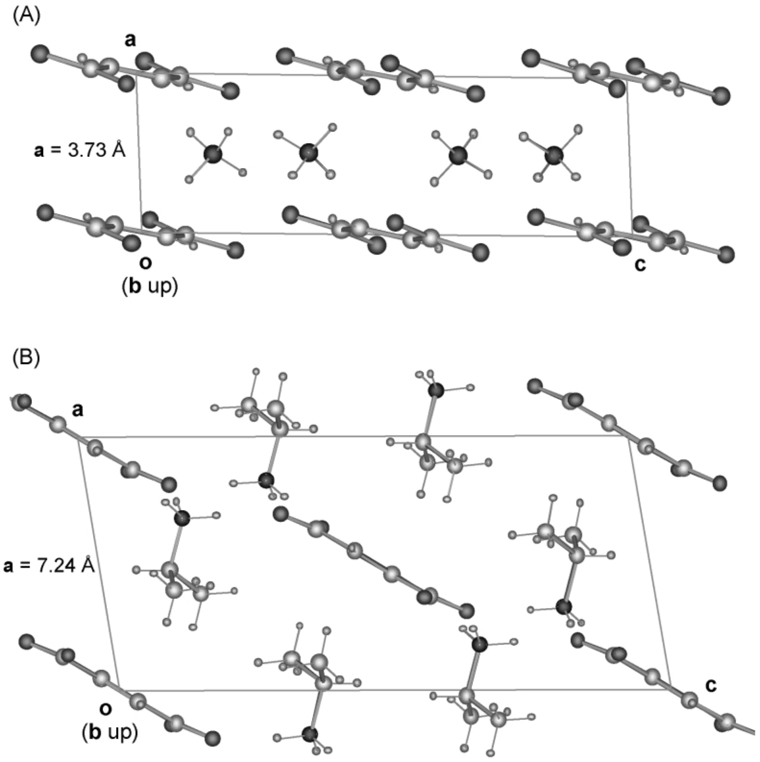


Figure 1. The crystal structures of (A) diammonium fumarate (**1h**) and (B) bis(isopropylammonium) fumarate (**1e**). The figures are somewhat modified from those reported in Ref. 12.

triethylamine (**m**), guanidine hydrochloride (**n**), imidazole (**A**), 1,2,4-triazole (**B**), pyridine (**C**), pyrazine (**D**), 2-aminopyrimidine (**E**), benzimidazole (**F**), quinoline (**G**), isoquinoline (**H**), acridine (**I**), *o*-methylcinnamic acid (**4**), *m*-methylcinnamic acid (**5**), *m*-methoxycinnamic acid (**6**), *p*-methoxycinnamic acid (**7**), *m*-chlorocinnamic acid (**8**), and *trans*-cinnamic acid (**9**), were purchased from the commercial sources.

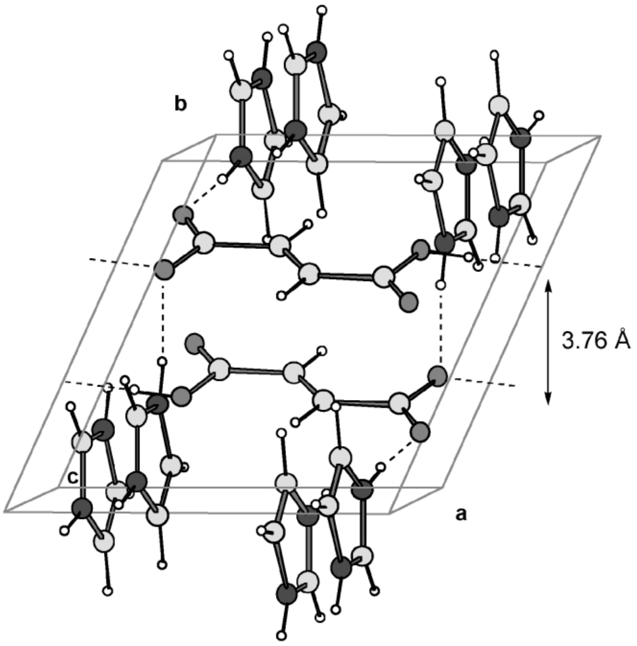


Figure 2. The crystal structure of imidazolium hydrogen fumarate (**1A**). Broken lines indicate hydrogen bonds.

4.3. Preparation of salt crystals

A warm solution containing 742 mg (6.39 mmol) of **1** in MeOH (10 mL) was mixed with a solution containing 871 mg (12.79 mmol) of imidazole (**A**) in MeOH (10 mL) and the hot mixture was filtered immediately. Upon cooling to room temperature, colorless prisms crystallized out of the filtrate and were collected by filtration to afford 793 mg (67%) of the salt **1A**. This was dried in vacuo at room temperature for 20 h and characterized by ^{1}H NMR (DMSO-d$_6$), IR (KBr), and elemental analyses. This crystal showed a complex melting behavior, starting to melt above 192°C, then resolidified around 210°C, and finally decomposed at 278–281°C. The NMR spectrum was a superposition of the spectra of **1** and **A**. A strong IR frequency corresponding to the CO_2^- group was observed at 1585 cm^{-1}. The molar ratio of the constituents was determined by the NMR and elemental analyses to be 1:1.

All the other salts were similarly prepared and characterized. Detailed data for the solvents which were used for mixing and recrystallization, mp, the molar ratio of the constituents, IR (1500–1650 cm^{-1} region), and the elemental analysis are summarized in Tables 4–9. From inspection of the IR data, **1m** as well as most of the salts of **1** with aromatic heterocyclic amines except **1A** showed no strong, broad absorption corresponding to the CO_2^- group at 1500–1650 cm^{-1} region. Therefore, these salts may be more appropriately called hydrogen-bonded cocrystals. However,

Table 4. Preparation of fumaric acid/amine salt crystals **1a–1n**, prepared from fumaric acid (**1**) and alkylamines **a–m** and guanidine hydrochloride (**n**)

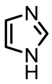
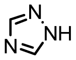
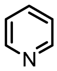
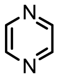
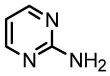
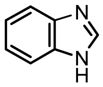
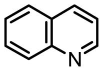
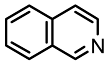
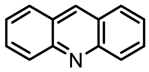
Salt	Amine	Solvent		Mp (°C)	**1**/amine[a]	IR frequency[b] (cm^{-}1)
		Mixing	Recrystzn[c]			
1a	*t*-BuNH$_2$	*i*-PrOH	EtOH+MeOH	>223 (sublim)	1:2	1555
1b	*s*-BuNH$_2$	EtOH	EtOH+Et$_2$O	166.5–168.5	1:2	1632, 1560, 1525
1c	(*S*)-*s*-BuNH$_2$	EtOH	EtOH+Et$_2$O	168–171	1:2	1632, 1560, 1525
1d	PrNH$_2$	EtOH	EtOH	163.5–167	1:2	1584, 1509
1e	*i*-PrNH$_2$	EtOH	EtOH	201–205	1:2	1560
1f	EtNH$_2$	EtOH+H$_2$O	EtOH+H$_2$O	185.5–187.5	1:2+0.1(H$_2$O)	1560, 1535
1g	MeNH$_2$	EtOH+MeOH+H$_2$O	EtOH+MeOH+H$_2$O	188–200	1:2	1559, 1538[d]
1h	NH$_3$	*i*-PrOH+H$_2$O	MeOH+H$_2$O[e]	243–254	1:2	1577
1i	PhCH$_2$NH$_2$	EtOH	MeOH	178–184	1:2	1566, 1526
1j	*t*-chxn	MeOH	MeOH+H$_2$O	>213 (unclear)	1:1	1587
1k	(*S*,*S*)-*t*-chxn	EtOH	MeOH+H$_2$O	212–221	1:1.05+0.16(H$_2$O)	1561
1l	*c*-chxn	EtOH	MeOH+H$_2$O	195–203	1:1+0.45(H$_2$O)	1586, 1560
1m	Et$_3$N	*i*-PrOH+Et$_2$O	*i*-PrOH+Et$_2$O	75–99	1:1	1632[d]
1n(1)	(H$_2$N)$_2$C=NH·HCl	MeOH+H$_2$O	MeOH, first crop	229–237 (dec)	8:1+0.5(H$_2$O)	Not measured
1n(2)			Second crop	208–226 (dec)	3.7:1+0.4(H$_2$O)	Not measured

[a] Molar ratios based on the elemental analysis (Table 7).
[b] 1500–1650 cm^{-1} region corresponding to the CO$_2^-$ and/or –NH$_3^+$ groups: in KBr, unless otherwise specified.
[c] The resultant crystals were dried in vacuo at room temperature, unless otherwise specified.
[d] In nujol.
[e] Air-dried at room temperature.

1m is a hydrogen fumarate, judging from the X-ray crystallographic structural analysis.[¶] So far, the crystal structures for **1e** (Fig. 1(B)),[12] **1h** (Fig. 1(A)),[12] **1m**,[14] and **1A** (Fig. 2) were determined. Further studies by the single crystal X-ray analysis are in progress, including those for several ammonium cinnamates.

4.3.1. Photoproducts. Irradiations were made under argon atmosphere in a vessel described previously,[2] with a 10 W low-pressure mercury lamp through quartz or with a 400 W high-pressure mercury lamp through Pyrex. Photolysates were analyzed by ^{1}H NMR (in DMSO-d$_6$) and characterized in general by direct comparison with authentic samples. The

Table 5. Preparation of aminium fumarates **1A–1I** from fumaric acid (**1**) and aromatic heterocyclic amines **A–I**

Salt	Amine	Solvent		Mp (°C)	**1**/amine[a]	IR frequency[b] (cm^{-1})
		Mixing	Recrystzn[c]			
1A		MeOH	MeOH	Unclear (>192)	1:1	1635, 1585
1B		MeOH	MeOH	183–208	1:1.06	1640, 1515
1C		MeOH	MeOH[d]	>242 (sublim)	1:1[e]	No evident peaks[f]
1D		MeOH	MeOH[d]	>230 (sublim)	1:0.86	No evident peaks[f]
1E		MeOH	MeOH	>244 (sublim)	1:1	1628, 1560
1F		MeOH	MeOH	182–184	1:1	1625, 1525
1G		MeOH	MeOH	>230 (sublim)	1:1	1644, 1595, 1508
1H		MeOH	MeOH	>215 (sublim)	1:1	1646
1I		MeOH	MeOH	194–202	1:2	1623, 1568, 1522

[a] Molar ratios based on the elemental analysis (Table 8), unless otherwise specified.
[b] 1500–1650 cm^{-1} region.
[c] The resultant crystals were dried in vacuo at room temperature.
[d] A part of the heterocyclic amine was lost on drying and the samples turned opaque.
[e] From NMR.
[f] In nujol.

Table 6. Preparation of ammonium *trans*-cinnamates **4h**–**9h** from *trans*-cinnamic acids **4**–**9** and ammonia (**h**)

Salt	R	Solvent		Mp[a] (°C)	Acid/NH_3[b]	IR frequency[c] (cm^{-}1)
		Mixing	Recrystzn[d]			
4h	*o*-Me	$MeOH+H_2O$	*i*-$PrOH+Et_2O+H_2O$	173–175	1:0.93	1525
5h	*m*-Me	$MeOH+H_2O$	$MeOH+H_2O$	116–120	1:0.97	1530
6h	*m*-OMe	$MeOH+H_2O$	*i*-PrOH	88–90	1:1	1520
7h	*p*-OMe	$MeOH+H_2O$	$MeOH+H_2O$	175–178	1:1	1535
8h	*m*-Cl	$MeOH+H_2O$	$MeOH+H_2O$	160–161	1:1	1520
9h	H	$MeOH+H_2O$	*i*-PrOH	133–135	1:0.82	1530

[a] The melting point for **4h**, **5h**, **7h**, **8h**, and **9h** is virtually the same as that of the corresponding parent acid. In fact, ammonia was slowly lost on exposure of 4 h–**9h** to air.

[b] Molar ratios based on the elemental analysis (Table 9).

[c] The absorption corresponding to the CO_2^- group: in nujol.

[d] The resultant crystals of **6h**–**9h** were dried in vacuo at room temperature for a short period of time (1–2 h), while those of **4h** and **5h** were only air-dried since NH_3 was especially easily lost.

authentic sample of *cis*,*trans*,*cis*-1,2,3,4-cyclobutanetetracarboxylic acid (CBTA) was obtained from the solid state photodimerization of dimethyl fumarate followed by hydrolysis with conc HCl.[15] Betaines **2** and **3** were prepared according to the literature method.[8] The stereochemistry of the truxinic or truxillic dimers of *trans*-cinnamic acids **4**–**8** was assigned on the basis of the characteristic ^{1}H NMR chemical shift and coupling pattern of the cyclobutyl protons.[4,6a,16] They were very similar to those of the dimers of unsubstituted *trans*-cinnamic acid (**9**), which were available from our previous work.[4] Dimethyl 2,2′-dimethyl-δ-truxinate (**10**), 3,3′-dimethyl-δ-truxinic acid (**11**), 3,3′-dimethyl-β-truxinic acid (**12**), and 3,3′-dimethoxy-δ-truxinic acid (**13**) were separated by preparative TLC on silica gel (MeOH–$CHCl_3$) or by preparative HPLC (Asahipak GS-320, MeOH) and their ^{1}H NMR, IR, and MS spectra are given below. 2,2′-Dimethyl-δ-truxinic acid was spontaneously esterified with methanol into the dimethyl ester **10** during the separation procedure.

Dimethyl 2,2′-dimethyl-δ-truxinate (**10**): ^{1}H NMR (DMSO-d$_6$, 270 MHz) δ 7.54 (2 H, d, J=8.5 Hz), 7.24 (2 H, t, J=8.5 Hz), 7.11 (2 H, t, J=8.5 Hz), 7.06 (2 H, d, J=8.5 Hz), 3.82 (2 H, quasi-d, J=9.7 Hz, cyclobutyl), 3.61 (6 H, s, CO_2Me), 3.48 (2 H, quasi-d, J=9.7 Hz, cyclobutyl), 1.96 (6 H, s, Me); IR (film) 1733 (CO_2Me), 1436, 1211, 1165, 755 cm^{-1}; MS (FAB$^+$, NBA) *m/z* (rel intensity) 353 (100, $(M+H)^+$), 176 (62), 145 (46, $[MeO_2CCH{=}CHCO_2Me+H]^+$); HRMS (FAB$^+$, NBA) calcd for $C_{22}H_{25}O_4$ 353.1753, found 353.1752 ($(M+H)^+$). 2,2′-Dimethyl-δ-truxinic acid exhibited ^{1}H NMR (DMSO-d$_6$, 270 MHz) peaks at δ 7.46–7.00 (8 H, m, aromatic), 3.44 (2 H, quasi-d, J=9.5 Hz, cyclobutyl), 2.99 (2 H, quasi-d, J=9.5 Hz, cyclobutyl), and 2.00 (6 H, s, Me). This compound was methylated with methanol during the chromatographic separation with silica gel, giving **10**.

Table 7. Analytical data for fumaric acid/amine salt crystals **1a**–**1n**, prepared from fumaric acid (**1**) and alkylamines **a**–**m** and guanidine hydrochloride (**n**)

	Calcd (%)[a]			Found (%)		
	C	H	N	C	H	N
1a	54.94	9.99	10.68	54.77	9.83	10.41
1b	54.94	9.99	10.68	54.82	9.79	10.60
1c	54.94	9.99	10.68	54.82	9.79	10.48
1d	51.26	9.46	11.96	51.17	9.24	11.90
1e	51.26	9.46	11.96	51.08	9.33	11.74
1f	46.19	8.82	13.46	46.19	8.88	13.46
1g	40.44	7.92	15.72	40.34	7.73	15.60
1h	32.00	6.71	18.66	31.81	6.53	18.46
1i	65.44	6.71	8.48	65.27	6.78	8.43
1j	52.16	7.88	12.17	51.92	8.02	12.10
1k	51.79	8.03	12.31	51.86	8.31	12.24
1l	50.39	7.99	11.75	50.41	7.86	11.48
1m	55.28	8.81	6.45	55.00	8.82	6.22
1n(1)	38.37 Cl, 3.43	3.80	4.07[b]	38.41 Cl, 3.39	3.86	4.14
1n(2)	35.66 Cl, 6.66	4.09	7.90[c]	35.67 Cl, 6.85	4.12	7.76

[a] See Table 4 for the **1**/amine ratio.

[b] $(\mathbf{1})_8((H_2N)_2C{=}NH{\cdot}HCl)_1(H_2O)_{0.5}$.

[c] $(\mathbf{1})_{3.7}((H_2N)_2C{=}NH{\cdot}HCl)_1(H_2O)_{0.4}$.

3,3′-Dimethyl-δ-truxinic acid (**11**): ^{1}H NMR (DMSO-d$_6$, 270 MHz) δ 7.18–6.95 (8 H, m, aromatic), 3.32 (2 H, quasi-d, J=9.2 Hz, cyclobutyl), 2.78 (2 H, quasi-d, J=9.2 Hz, cyclobutyl), 2.25 (6 H, s, Me); IR (KBr) 1700 (CO_2H), 1606, 1564, 1411, 1252, 1021, 782, 700 cm^{-1}; MS (FAB$^+$, DTT/TG) *m/z* (rel intensity) 325 (21, $(M+H)^+$), 209 (100, $[MeC_6H_4CH{=}CHC_6H_4Me+H]^+$); HRMS (FAB$^-$, TEA) calcd for $C_{20}H_{19}O_4$ 323.1283, found 323.1288 ($(M-H)^-$).

3,3′-Dimethyl-β-truxinic acid (**12**): ^{1}H NMR (DMSO-d$_6$, 270 MHz) δ 6.93 (2 H, t, J=7.7 Hz), 6.83 (2 H, s), 6.79 (4 H, d, J=7.7 Hz), 3.98 (2 H, quasi-d, J=6.6 Hz, cyclobutyl), 3.55 (2 H, quasi-d, J=6.6 Hz, cyclobutyl), 2.12 (6 H, s, Me); IR (KBr) 1716 (CO_2H), 1606, 1409, 1226, 779, 699 cm^{-1}; MS (FAB$^+$, TEA) *m/z* (rel intensity) 325 (56, $(M+H)^+$), 209 (100, $[MeC_6H_4CH{=}CHC_6H_4Me+H]^+$); HRMS (FAB$^+$, TEA) calcd for $C_{20}H_{21}O_4$ 325.1440, found 325.1439 ($(M+H)^+$).

3,3′-Dimethoxy-δ-truxinic acid (**13**): white solid, mp 224–226 °C (from $CHCl_3$): ^{1}H NMR (DMSO-d$_6$, 270 MHz) δ

Table 8. Analytical data for aminium fumarates **1A**–**1I**, prepared from fumaric acid (**1**) and aromatic heterocyclic amines **A**–**I**

	Calcd (%)[a]			Found (%)		
	C	H	N	C	H	N
1A	45.66	4.38	15.21	45.52	4.45	15.50
1B	38.84	3.82	23.53	38.66	3.87	23.55
1D	48.32	4.05	13.03	48.32	4.08	13.00
1E	45.50	4.30	19.90	45.71	4.17	20.18
1F	56.41	4.30	11.96	56.30	4.40	11.92
1G	63.67	4.52	5.71	63.78	4.41	5.78
1H	63.67	4.52	5.71	63.69	4.43	5.63
1I	75.94	4.67	5.90	76.22	4.79	5.89

[a] See Table 5 for **1**/amine ratio.

Table 9. Analytical data for ammonium *trans*-cinnamates **4h**–**9h**, prepared from *trans*-cinnamic acids **4**–**9** and ammonia (**h**)

Salt	Calcd (%)[a]			Found (%)		
	C	H	N	C	H	N
4h	67.47	7.24	7.32	67.20	7.20	7.17
5h	67.21	7.28	7.60	67.17	7.09	7.54
6h	61.53	6.71	7.18	61.42	6.62	6.99
7h	61.53	6.71	7.18	61.45	6.58	7.13
8h	54.15 Cl, 17.76	5.05	7.02	54.39 Cl, 17.81	5.02	6.97
9h	66.68	6.50	7.08	66.73	6.52	7.11

[a] See Table 6 for the acid/NH_3 ratio.

7.16 (2 H, t, J=8.0 Hz), 6.90 (2 H, s), 6.87 (2 H, d, J=8.0 Hz), 6.73 (2 H, d, J=8.0 Hz), 3.72 (6 H, s, OMe), 3.32 (2 H, quasi-d, J=9.5 Hz, cyclobutyl), 2.77 (2 H, quasi-d, J=9.5 Hz, cyclobutyl); IR (KBr) 1720 (CO_2H), 1607, 1580, 1290, 1054, 779, 696 cm^{-1}; MS (FAB^+, DTT/TG) m/z (rel intensity) 357 (100, $(M+H)^+$), 241 (88, $[MeOC_6H_4CH{=}CHC_6H_4OMe+H]^+$); HRMS ($FAB^-$, TEA) calcd for $C_{20}H_{19}O_6$ 355.1182, found 355.1190 ($(M-H)^-$).

4.4. Determination of the X-ray crystal structure of 1A

X-Ray intensities were measured on MacScience DIP2030K diffractometer (IP radius 150 mm) with graphite monochromatized MoKα radiation (λ=0.71073 Å). The structure was solved and refined using maXus. Crystal data: $C_7H_8O_4N_2$, M=184.151, triclinic, $P\bar{1}$ a=7.4860(5), b=7.7590(3), c=8.4290(6) Å, α=69.710(4)°, β=81.403(4)°, γ=66.168(4)°, V=420.03(5) $Å^3$, Z=2, D_x=1.456 g/cm^3, μ=0.121 mm^{-1}, 1826 measured reflections, R=0.042, R_w=0.098 for 1707 reflections [$I > 3\sigma(I)$ with 151 parameters]. Crystallographic data for **1A** have been deposited with the Cambridge Crystallographic Data Center, deposition number 206967. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

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