Photoisomerization of ammonium α,β-unsaturated carboxylates in the solid state: effect of the hydrogen-bond network on the reactivity

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EZ-Photoisomerization has been attained for several kinds of salts of α,β-unsaturated carboxylic acids with amines. This photoreaction has been proven to be an effective method for preparing (Z)-isomers from ammonium (E)-α,β-unsaturated carboxylates. The isomerizability is strikingly altered upon changing the ammonium group, which implies that the crystal structure affected the reactivity to a considerable extent. However, the cavity in the crystal has been found to have less influence than expected on the isomerizability. A further detailed study concerning the crystal structures suggested that the characteristics of the hydrogen-bond network had a close correlation with the isomerizability. Moreover, both the bulkiness of the carboxylate and ammonium groups as well as their difference in molecular length are considered to be the most important factors influencing the isomerizability.

In recent years reaction media have been considered to be important for controlling the regio- and/or stereo-selectivity in organic synthetic reactions.[1] Among them, the crystalline state has been attracting much attention, since it gives the most ordered and rigid environment, and many intriguing results have been reported concerning solid state reactions up to now.[2] Most of these solid state reactions are promoted by photoirradiation to yield [2 + 2] photocycloadducts,[3] Norrish type-II hydrogen-abstracted products,[4] and so on.[5] However, the photoisomerization of the carbon–carbon double-bond (*EZ*-isomerization), which is one of the most popular and fundamental photoreactions in solution, is still rare compared with other photoreactions in the solid state.[6] Since the dynamic movement of a molecule, which is disadvantageous for a crystalline-state reaction, is required for *EZ*-isomerization, only a few reports have discussed the reactivity of *EZ*-isomerization in the solid state for non-systematically selected compounds.[7] Therefore, the general features of the reaction, especially concerning the relationship between the reactivity and the crystal structure, are still unknown in detail.

During the course of our study concerning the topochemical photoreaction of olefinic compounds in the solid state, we found that (±)-1-phenylethylammonium (*E*)-3-phenylpent-2-enoate *E*-**1a** underwent an *EZ*-isomerization reaction selectively in the solid state to give its (*Z*)-isomer (*Z*-**1a**) in high yield. This result indicates two interesting aspects: the reaction behaviour would be controlled by a modification of the ammonium salt, and the features of the reaction could be systematically studied using various kinds of ammonium salts. One of the most serious disadvantages in solid state reactions is difficulties encountered optimizing the reaction conditions, compared with other synthetic organic reactions in solution. In contrast, the use of various kinds of ammonium salts, which offer different reaction environments from each other in the solid state, would give one solution to this problem for the case of the *EZ*-isomerization of an α,β-unsaturated carboxylic acid. It is also expected that photoisomerization would be applicable to general α,β-unsaturated carboxylic acids.

Here, we report on the *EZ*-isomerization of ammonium α,β-unsaturated carboxylates in the solid state, and discuss the relationship between the reaction behaviour and the molecular and/or crystal structures of the salts.

Results and discussion

Photoreaction of ammonium α,β-unsaturated carboxylates in the solid state

When crystalline (±)-1-phenylethylammonium (*E*)-3-phenylpent-2-enoate *E*-**1a** was irradiated in the solid state with a 500 W super-high-pressure mercury lamp for 24 h at room temperature, the crystalline (*Z*)-isomer *Z*-**1a** was obtained in 80% yield; neither the [2 + 2] cycloadduct nor the Norrish type-II hydrogen-abstracted product was detected by a ^1H NMR analysis. Since *EZ*-isomerization in the solid state is rather rare compared with other photochemical reactions, such as the [2 + 2] cycloaddition reaction[3] and the Norrish type-II hydrogen abstraction,[4] the fact that *E*-**1a** selectively isomerized upon photoirradiation in the solid state prompted us to study the reaction in detail.

Based on a consideration that the photoisomerizability of the (*E*)-3-phenylpent-2-enoate anion could be controlled by a modification of the ammonium group of *E*-**1a**, we carried out the photoirradiation of *E*-**1b–d** in the same way as that for *E*-**1a**. At the same time we performed a solid state photoreaction of some ammonium salts of the (*Z*)-isomer of *E*-**1** (*Z*-**1**) (Table 1). As a result, the reactivity of *E*-**1** in the solid state considerably altered upon changing the ammonium group. In contrast, the crystalline salts of *Z*-**1** were found to have extremely low reactivity.

When the reaction of *E*-**1a** in the solid state was monitored by the changes in the X-ray powder-diffraction pattern, a progressive formation of the crystal of *Z*-**1a** was observed† (Fig. 1). The different photoreactivities of *Z*-**1a** from *E*-**1a** and the change in the X-ray powder-diffraction pattern indicate that

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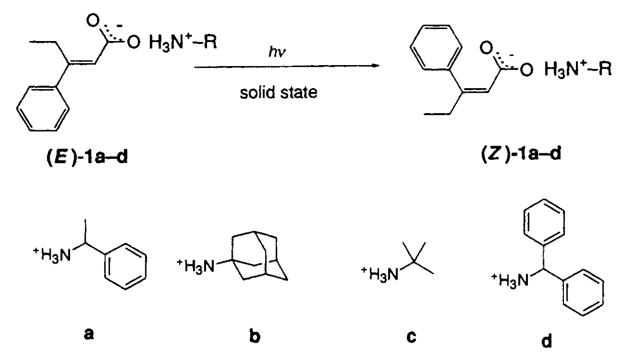
† The X-ray powder-diffraction pattern of *Z*-**1a** in Fig. 1 was consistent with its lattice constants.

Table 1 *EZ*-Isomerization of ammonium salts of *E*-**1** in the solid state



Salt	Ammonium group	*E*:*Z* ratio[a]
E-**1a**	**a**	20:80
E-**1b**	**b**	40:60
E-**1c**	**c**	86:14
E-**1d**	**d**	92:8
Z-**1a**	**a**	0:100
Z-**1b**	**b**	0:100
Z-**1c**	**c**	0:100
Z-**1d**	**d**	7:93

[a] The ratio was determined by a ^{1}H NMR analysis after irradiation for 24 h with a 500 W super-high-pressure mercury lamp under an argon atmosphere.

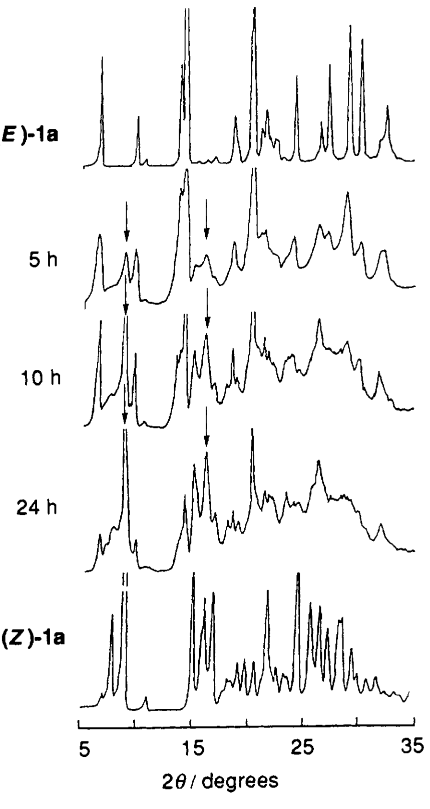
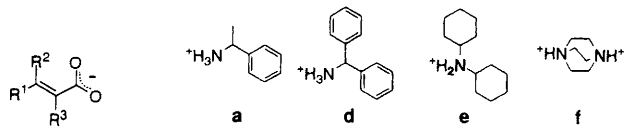


Fig. 1 Change in the X-ray powder-diffraction pattern of *E*-**1a** with photoirradiation. The pattern of *Z*-**1a** is also depicted as a reference. The peaks which newly appeared upon photoirradiation are indicated by arrows, which coincide with those of *Z*-**1a**.

the *EZ*-isomerization of *E*-**1a** proceeds irreversibly to form the (*Z*)-isomer, and is a crystal-to-crystal transformation.

Next, we applied the solid state photoreaction to various kinds of ammonium salts of α,β-unsaturated carboxylic acids (Table 2). (*Z*)-Isomers could be obtained from many kinds of ammonium salts of (*E*)-α,β-unsaturated carboxylic acids upon photoirradiation in the solid state. In most cases, only *EZ*-isomerization occurred; other reactions, such as the Norrish type-II reaction and the [2 + 2] photocycloaddition, did not proceed. Only *E*-**8f**, exceptionally, gave a Norrish type-II product, which was detected by a ^{1}H NMR analysis of the photoproduct.

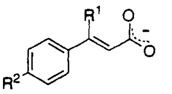
Table 2 *EZ*-Isomerization of ammonium salts of α,β-unsaturated carboxylic acids in the solid state



Salt	R^1	R^2	R^3	Ammonium group	*E*:*Z* ratio[a]
E-**2a**	Ph	H	H	**a**	100:0
E-**2f**				**f**[b]	100:0
E-**3a**	Ph	Me	H	**a**	6:94
E-**3d**				**d**	33:67
E-**4a**	Ph	H	Me	**a**	62:38
E-**4f**				**f**[b]	100:0
E-**5a**	Me	H	H	**a**	77:23
E-**5f**				**f**[b]	81:19
E-**6a**	Me	H	Me	**a**	85:15
E-**6e**				**e**	100:0
E-**7e**	Bu^t	H	H	**e**	74:26
E-**7f**				**f**[b]	63:37
E-**8e**	Bu^t	Me	H	**e**	39:61
E-**8f**				**f**[b]	37:63[c]

[a] The ratio was determined by a ^{1}H NMR analysis after irradiation for 24 h with a 500 W super-high-pressure mercury lamp at room temperature under an argon atmosphere. [b] Two equivalents of the carboxylic acid were used for preparing the salt. [c] Norrish type-II product was obtained in 44% yield.

Table 3 Effect of substituent(s) on the isomerizability in the solid state



Salt	R^1	R^2	*E*:Z ratio[a]
E-**3a**	Me	H	6:94
E-**1a**	Et	H	20:80
E-**9a**	Pr^i	H	70:30
E-**10a**	c-Hexyl	H	97:3
E-**11a**	Et	Me	67:33
E-**12a**	Et	Cl	83:17
E-**13a**	Et	Bu^t	88:12

[a] Photoirradiation was performed for 24 h using a 500 W super-high-pressure mercury lamp at room temperature under an argon atmosphere. The product ratio was determined by a ^{1}H NMR analysis.

In each case, the isomerizability of ammonium α,β-unsaturated carboxylates in the solid state was strongly affected by a change in the ammonium group, as was that of the *E*-**1** derivatives. A typical example was the photoreaction of *E*-**4**; the salt with (±)-1-phenylethylamine (*E*-**4a**) afforded the (*Z*)-isomer in 38% yield, whereas the salt with 1,4-diazabicyclo[2.2.2]octane (*E*-**4f**) afforded no (*Z*)-isomer upon photoirradiation. The best result was attained for the photoirradiation of (±)-1-phenylethylammonium 3-phenylbut-2-enoate (*E*-**3a**) to afford the (*Z*)-isomer in 94% yield.

We also performed the photoirradiation of (±)-1-phenylethylammonium salts of α,β-unsaturated carboxylic acids having an arenyl group with a substituent of differing bulkiness at the *p*-position and/or a substituent at the β-position in order to investigate the relationship between the isomerizability and chemical structure (Table 3). It is noteworthy that the yield of the (*Z*)-isomer precisely depends on the bulkiness of the substituents; the salts with a smaller substituent(s) resulted in an increased formation of the (*Z*)-isomer.

Table 4 Summary of the crystal data of ammonium α,β-unsaturated carboxylates

	Salt						
	E-**1a**[a]	*E*-**1b**[b]	*E*-**1c**	*E*-**1d**	*E*-**9a**	*E*-**10a**	*E*-**11a**
Formula	$C_{19}H_{23}N_1O_2$	$C_{21}H_{29}N_1O_2$	$C_{15}H_{23}N_1O_2$	$C_{23}H_{25}N_1O_2$	$C_{20}H_{25}N_1O_2$	$C_{23}H_{29}N_1O_2$	$C_{20}H_{25}N_1O_2$
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
Space group	Pn	$C2/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$P2_1/a$
a/Å	19.011(3)	32.274(3)	15.857(4)	24.146(3)	6.0014(6)	20.794(6)	19.717(6)
b/Å	6.444(1)	6.6125(8)	6.739(2)	12.720(2)	10.824(1)	6.507(2)	6.395(1)
c/Å	14.938(3)	17.394(2)	15.007(4)	6.620(1)	14.516(2)	15.844(4)	14.649(3)
α/°					93.30(1)		
β/°	110.30(1)	95.100(9)	106.69(2)	95.37(1)	96.79(1)	100.38(2)	91.07(2)
γ/°					103.43(1)		
V/Å^3	1716.3(5)	3697.3(7)	1536.1(7)	2024.3(4)	907.2(2)	2109(1)	1846.7(7)
Z	4	8	4	4	2	4	4
F(000)	640	1424	544	768	336	760	672
D_c/g cm^{-3}	1.15	1.17	1.08	1.18	1.14	1.11	1.12
μ/cm^{-1}	5.11	5.08	4.90	5.10	5.00	4.75	4.92
Crystal size/mm	0.4 × 0.4 × 0.2	0.4 × 0.2 × 0.2	0.6 × 0.3 × 0.1	0.4 × 0.3 × 0.3	0.6 × 0.1 × 0.1	0.5 × 0.3 × 0.1	0.8 × 0.2 × 0.1
No. of parameters	507	424	225	344	284	323	286
Used reflections[c]	2145	2278	1875	2766	2686	3997	1578
R	0.070	0.058	0.066	0.053	0.082	0.090	0.070
R_w	0.075	0.071	0.078	0.065	0.086	0.065	0.084
Max. e Å^{-3}	0.17	0.19	0.22	0.19	0.21	0.20	0.20
Direct methods	MULTAN	SHELXS 86	MULTAN	MULTAN	MULTAN	MULTAN	MULTAN

	E-**12a**	*E*-**13a**	*Z*-**1a**†	*Z*-**1c**	*Z*-**1d**	*Z*-**9a**
Formula	$C_{19}H_{22}N_1O_2Cl_1$	$C_{23}H_{31}N_1O_2$	$C_{19}H_{23}N_1O_2$	$C_{15}H_{23}N_1O_2$	$C_{24}H_{25}N_1O_2$	$C_{20}H_{21}N_1O_2$
Crystal system	monoclinic	triclinic	triclinic	tetragonal	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$I\bar{4}$	$P2_1/a$	$P\bar{1}$
a/Å	18.5291(5)	6.707(1)	6.475(6)	21.603(2)	13.624(2)	6.448(3)
b/Å	6.854(1)	9.954(2)	13.133(3)	21.603(2)	24.844(3)	13.770(4)
c/Å	14.728(5)	16.754(4)	20.896(5)	6.474(1)	13.450(1)	22.117(6)
α/°		90.42(2)	97.27(2)			106.55(2)
β/°	104.29(2)	90.57(2)	91.67(4)		116.7(8)	93.49(3)
γ/°		102.55(1)	97.88(4)			81.83(3)
V/Å^3	1812.4(8)	1091.7(3)	1744(2)	3021.2(9)	4088.8(8)	1863(1)
Z	4	2	4	8	8	4
F(000)	704	384	640	1087	1536	672
D_c/g cm^{-3}	1.21	1.07	1.13	1.09	1.17	1.11
μ/cm^{-1}	18.30	4.59	5.03	5.37	5.05	4.88
Crystal size/mm	0.3 × 0.3 × 0.3	0.9 × 0.4 × 0.1	0.6 × 0.4 × 0.2	2.0 × 0.05 × 0.05	0.6 × 0.2 × 0.2	0.5 × 0.2 × 0.2
No. of parameters	296	282	517	186	665	536
Used reflections[c]	2291	1306	3289	1070[d]	4438	3113
R	0.067	0.084	0.060	0.043	0.056	0.066
R_w	0.084	0.092	0.078	0.044	0.065	0.075
Max. e Å^{-3}	0.27	0.21	0.33	0.14	0.21	0.50
Direct methods	MULTAN	MULTAN	SHELXS 86	SIR 92	MULTAN	SHELXS 86

[a] Data were collected at 195 K. [b] Data were collected at 120 K. [c] $F \geqslant 3\sigma(F)$. [d] $F \geqslant 2.5\sigma(F)$.

Effect of the crystal structure on the isomerizability

From the experimental results which showed that the isomerizability of ammonium α,β-unsaturated carboxylates in the solid state was notably altered upon changing both the ammonium group and the substituent at the *p*-position of the β-arenyl group and/or at the β-position, it was suggested that the isomerizability was influenced by the molecular arrangement in the salts. In order to explain the phenomenon clearly, the crystal structures of some salts were determined by X-ray crystallographic analyses (Table 4).

One factor that may influence the isomerizability in the solid state, and which should be considered first, is a vacancy in the crystal, as reported in numerous previous studies concerning single-crystal-to-single-crystal transformation reactions,[8] since a dynamic movement of a molecule is required for *EZ*-isomerization. We therefore calculated the packing coefficients in each salt using the program OPEC.[9] The packing coefficients were calculated in two ways. One was in terms of the whole crystal (P_{whole}); the other was in terms of the local area around a carboxylate (P_{local}).

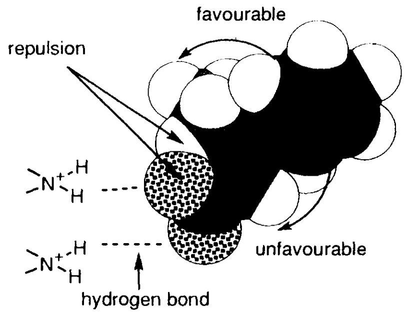


Fig. 2 Favourable direction of rotation for *E*-**1** derivatives

Concerning P_{local}, the calculation region was determined as follows. Since the hydrogen bonds between the carboxylate oxygens and the ammonium nitrogens are supposed to be very tight (as discussed later), isomerization would proceed with fixing of the position of the carboxylate oxygens. Therefore, isomerization is considered to proceed mainly by a rotation of the β-substituent(s) of the carboxylate. In addition, since one of the carboxylate oxygens sterically disturbs the rotation of the substituent(s) in a certain direction, especially for the *E*-**1** derivatives, the direction of rotation was judged to occur in one direction, as shown in Fig. 2. On the basis of these considerations, quarter-spherical regions, which had a common

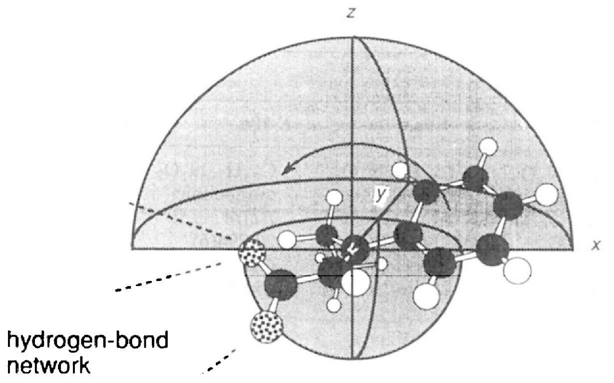


Fig. 3 Quarter spherical regions (shaded) for calculating the packing coefficient using the program OPEC. The olefinic plane is placed on the *xy*-plane, and the double bond is located parallel to the *y*-axis. The *z*-axis stands on the β-carbon. The radii of the spheres have been adjusted to the length of the substituents.‡

Table 5 Volume of the substituents and packing coefficients of *E*-**9a**–*E*-**12a**

Salt	V^a/Å^3	P_{whole}	P_{local}	*E*:*Z* ratio
E-**9a**	130.1	0.71	0.48	70:30
E-**10a**	163.2	0.70	0.56	97:3
E-**11a**	128.7	0.67	0.58	67:33
E-**12a**	129.6	0.70	0.62	83:17

[a] Sum of the volume of the substituents on the β-carbon of the carboxylate.

Table 6 Volume of the substituents and packing coefficients of *E*-**1a**, **c** and **d**

Salt	V^a/Å^3	P_{whole}	P_{local}	*E*:*Z* ratio
E-**1a**	112.3[b]	0.70	0.52	20:80
E-**1c**	112.4	0.66	0.48	86:14
E-**1d**	112.2	0.68	0.48	92:8

[a] Sum of the volume of the substituents on the β-carbon of the carboxylate. [b] Average value of two molecules in an asymmetric unit.

centre at the β-carbon of the carboxylate and radii adjusted to the length of the substituents,‡ were selected for an actual calculation, as depicted in Fig. 3.

Fig. 4 shows plots of the yield of the (*Z*)-isomer after 24 h irradiation *versus* P_{whole} and P_{local}. As can be seen, there is no distinct correlation between the packing coefficients and the yield of the (*Z*)-isomer. This result is far from a generally accepted explanation that a small packing coefficient results in a high reactivity in the solid state.[8] Regarding *E*-**9a**–**12a**, although the packing coefficients (P_{whole} and P_{local}) are similar, the difference in the volume of the substituents on the β-carbon is much greater than that in the packing coefficients (Table 5); the isomerizability of *E*-**9a**–**12a** seems to depend simply on the volume of the substituents. However, the absence of a correlation between the volume of the substituents and the isomerizability for the *E*-**1** salts (Table 6) indicates that this interpretation is not necessarily true.

From these results, we considered that another factor must exist, which would determine the isomerizability of the salt of an α,β-unsaturated carboxylic acid and an amine. We focused our attention on a columnar hydrogen-bond network as a possible factor, since all of the salts studied in the present work commonly had a characteristic columnar hydrogen-bond network between the carboxylate oxygens and the ammonium nitrogens in the solid state, as did those in our previous reports.[10] We then investigated the structure of the hydrogen-bond column in detail.

Role of the hydrogen-bond network on the isomerizability

The hydrogen-bond network of ammonium α,β-unsaturated carboxylates consists of units, formed from two pairs of the acid molecules and the amine molecules; the pairs are generally related to each other in a unit by an inversion centre or a two-fold screw axis. The units have hydrogen bonds with translational neighbouring units, and consequently form a columnar structure. A typical structure is shown in Fig. 5. In the hydrogen-bond column, both carboxylate oxygens and the ammonium nitrogens are tightly fixed. This tight fixation is strongly supported by the fact that the thermal factors of the carboxylate oxygens and ammonium nitrogens in the X-ray crystallogram are somewhat smaller than those of other elements. All of the salts of the (*Z*)-isomers, for which we could determine the crystal structures, also have a similar hydrogen-bond network to that of the corresponding (*E*)-isomers (Fig. 6). These facts suggest that the columnar hydrogen-bond network is preserved to a large extent during the course of the isomerization.

Upon carrying out a detailed study on the hydrogen-bond columns of ammonium (*E*)-α,β-unsaturated carboxylates and their (*Z*)-isomers, two structural characteristics, which seemed to influence the isomerization, were found. The first characteristic is the similarity in the topological structures of the hydrogen-bond columns between the (*E*)- and (*Z*)-isomers. The topological structures of the hydrogen-bond columns of highly photoreactive *E*-**1a** and its photoproduct *Z*-**1a** are quite similar. As a result, the change in alignment of the hydrogen-bond columns during the isomerization of *E*-**1a** into *Z*-**1a** is very small [Fig. 7: the inter-columnar distances (d_1 and d_2), the angle between them (θ) and the length of *a*, *b*, or *c* (d_3), which is parallel to the axis of the hydrogen-bond column, are listed in Table 7]. This fact indicates that the isomerization proceeds with a small change in the whole crystal structure; such a small change would be favourable for isomerization. In contrast, in the transformation from *E*–**1c** to *Z*–**1c**, the change in the alignment of the hydrogen-bond columns during the isomerization is very large, as can be seen from Fig. 8, which would arise from a large difference in length between the carboxylate and ammonium parts, unlike *E*–**1a**. Such a large change in the packing alignment of the hydrogen-bond columns in the crystal along with isomerization is considered to be unfavourable for a reaction in the solid state. Similarly, the relatively low isomerizability of *E*–**11a**–**13a** could be explained by the greater difference in length between the carboxylate and ammonium groups when a substituent is introduced at the *p*-position of the aromatic ring of the carboxylates.

The second characteristic is a difference in the packing around the carboxylate group. In the case of highly photoreactive *E*-**1a**, the carboxylate group is loosely pushed to the hydrogen-bond column, indicating that the hydrogen-bond column is hardly destroyed during isomerization. In contrast, the ammonium group of *E*-**1d**, which had low isomerizability regardless of the small difference in molecular length between the carboxylate and ammonium groups, forces the carboxylate group closer to the hydrogen-bond column upon replacing the methyl group of the ammonium group of *E*-**1a** by a phenyl group (Fig. 9). This implies that a considerable destruction of the hydrogen-bond column is required along with isomerization, which is energetically disadvantageous. Furthermore, for *E*-**9a** and *E*-**10a**, which also had low isomerizability, the bulky

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‡ The radii of the spheres used were 8.0 Å for the aromatic groups of *E*-**11a** and *E*-**12a**, 6.0 Å for the phenyl and alkyl groups of *E*-**10a** and 4.0 Å for the ethyl and/or other alkyl groups of the other salts.

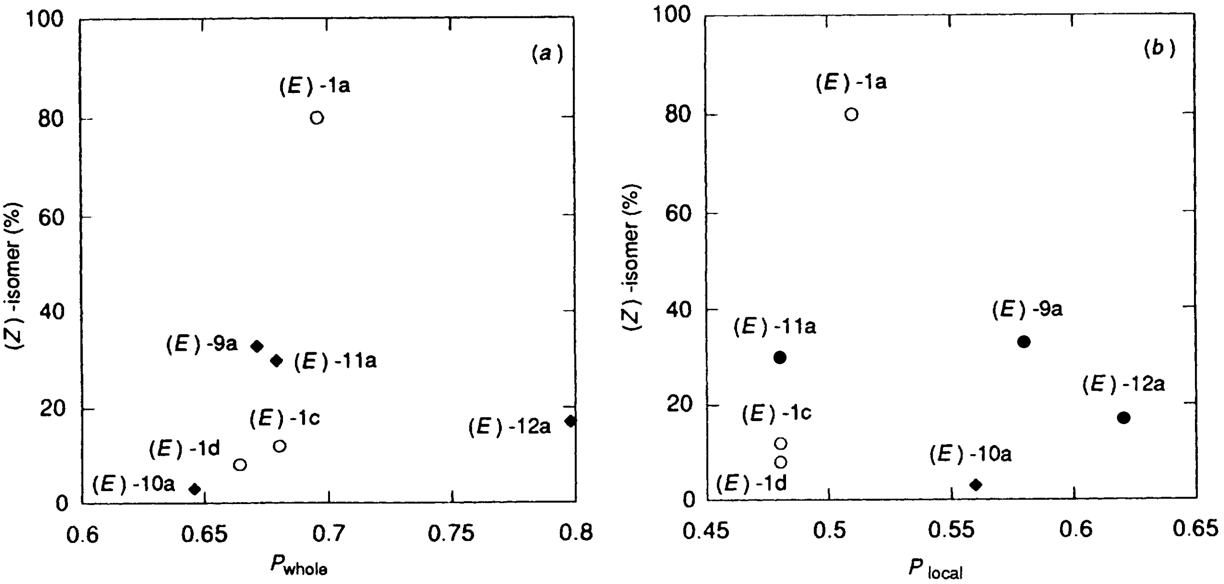

Fig. 4 Correlation between the packing coefficient and the yield of the (*Z*)-isomer after 24 h irradiation. Plots of the yield of the (*Z*)-isomer *vs.* P_{whole} (*a*) and *vs.* P_{local} (*b*).

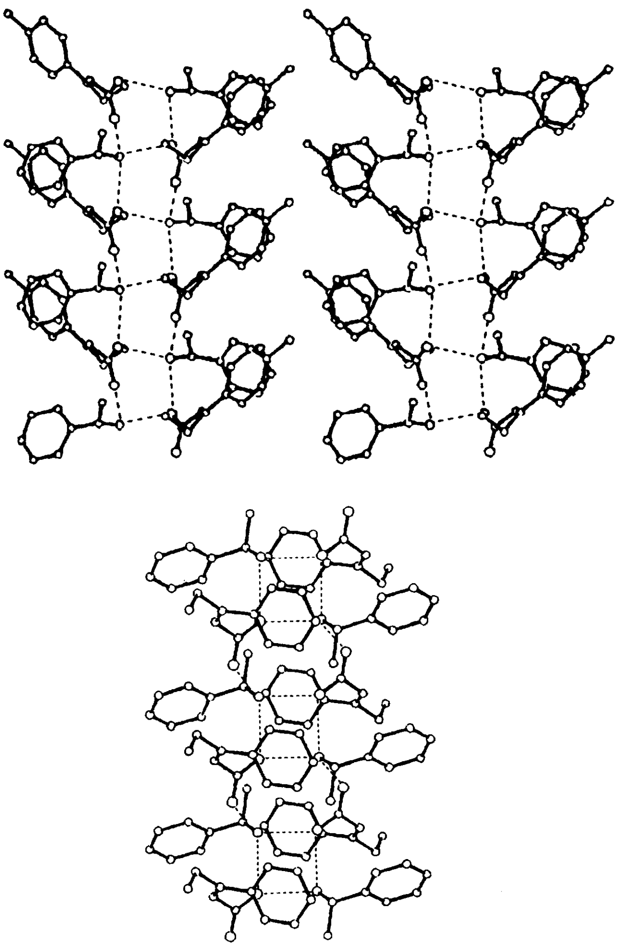

Fig. 5 Stereoview of the hydrogen-bond column of *E*-**12a**, which has a two-fold screw axis in the centre of the column. The dotted lines show the hydrogen bonds.

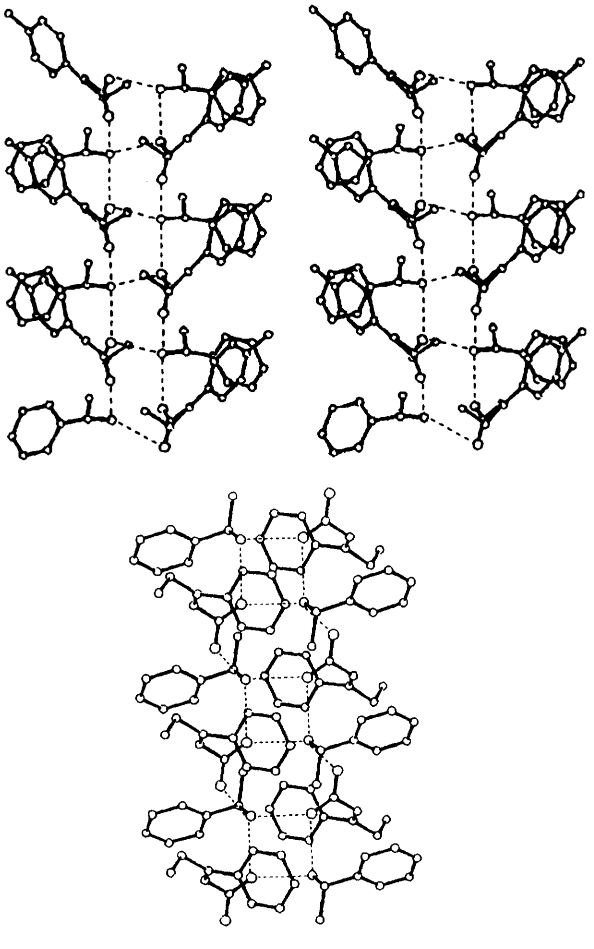

Fig. 6 Stereoview of the hydrogen-bond column of *Z*-**1a**. The dotted lines show the hydrogen bonds.

substituent on the β-carbon of the carboxylate group is close to the other molecules in the same hydrogen-bond column. These facts indicate that the bulkiness on both the carboxylate and ammonium groups has an influence on the isomerizability.

Thus, isomerizability of the ammonium salt of an α,β-unsaturated carboxylate is considered to be controlled by the following two factors. (*a*) The difference in molecular length between the carboxylate and ammonium groups: a small difference in molecular length leads to a small change in the topological structure of the hydrogen-bond column during the isomerization, and (*b*) the bulkiness of the carboxylate and ammonium groups: less bulky groups lead to loose packing around the carboxylate group in the hydrogen-bond column.

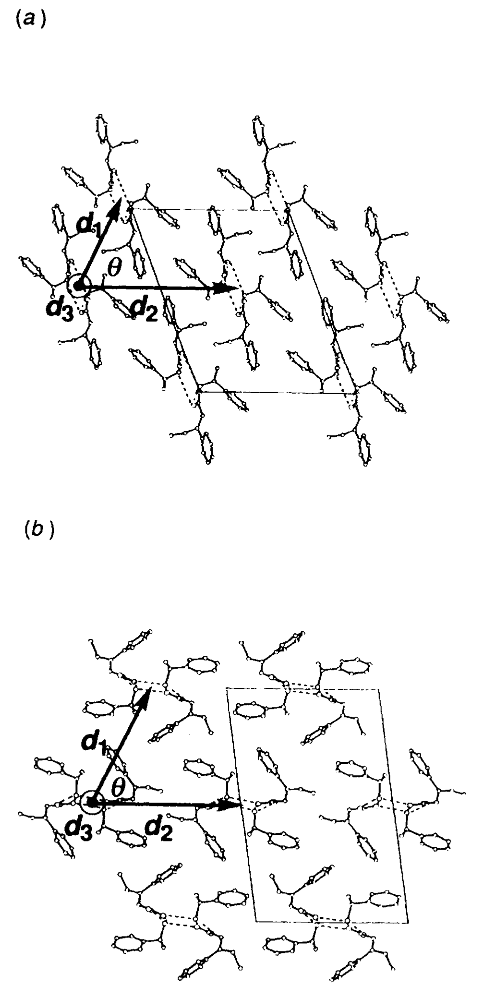

Fig. 7 Crystal structures of (*a*) *E*-**1a** and (*b*) *Z*-**1a** viewed down the axis of the hydrogen-bond column. The dotted lines show the hydrogen bonds. The arrows represent the vectors to the two nearest-neighbouring columns; d_1 and d_2 are the distances to them, and θ is the angle between them. d_3 is the length of the unit cell (*a*, *b* or *c*), which is parallel to the axis of the hydrogen-bond column.

Conclusions

The *EZ*-isomerization of ammonium α,β-unsaturated carboxylates in the solid state proceeded selectively from the (*E*)-isomer to the (*Z*)-isomer for the salts of various carboxylates. It is shown to be an effective method for preparing the corresponding (*Z*)-isomers. X-Ray crystallographic analyses suggested that the structure of the hydrogen-bond network of the salts affected their isomerizability to a considerable extent. Both the bulkiness of the carboxylate and ammonium groups and their difference in molecular length were found to be important factors which affect the isomerizability.

Experimental

General

Infrared spectra were recorded on a Jasco IR-810 spectrophotometer, and ^{1}H NMR spectra were measured on a JEOL PMX-60SI or a JEOL GX-400 instrument. The melting points were measured using a Laboratory Devices Mel-Temp, and are uncorrected. X-Ray powder-diffraction patterns were recorded with a Rigaku Rotaflex RU-200 spectrometer (λ = 1.5418 Å).

Crystals structure determination and refinement

Crystals for X-ray analyses were prepared by slow evaporation of the solvent (EtOH–H_2O) from saturated solutions in all cases. The X-ray intensities were measured up to $2\theta = 130°$ with graphite-monochromated Cu-Kα radiation ($\lambda = 1.5418$ Å) on a Mac Science MXC18 four-circle diffractometer by a 2θ–ω scan. All of the data were collected at room temperature, except for *E*–**1a** (at 195 K) and *E*–**1b** (at 120 K). The cell dimensions were determined from about 20 reflections ($50° < 2\theta < 60°$). The intensities and orientation of the crystals were checked by three standard reflections every 100 reflections.

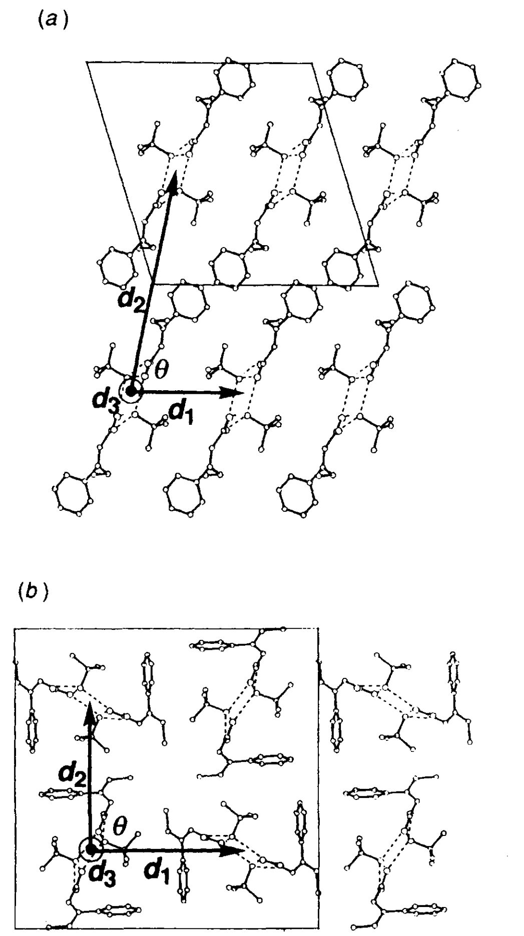

Fig. 8 Crystal structures of (*a*) *E*-**1c** and (*b*) *Z*-**1c** viewed down the axis of the hydrogen-bond column. The dotted lines show the hydrogen bonds. The arrows represent the vectors to the two nearest-neighbouring columns; d_1 and d_2 are the distances to them, and θ is the angle between them. d_3 is the length of the unit cell (*a*, *b* or *c*), which is parallel to the axis of the hydrogen-bond column.

Table 7 Distances and angles between hydrogen-bond columns

Salt	d_1/Å	d_2/Å	d_3[a]/Å	θ/°
E-**1a**	9.84	14.94	6.44	64.92
Z-**1a**	11.62	13.13	6.48	63.16
E-**1c**	7.50	15.47	6.74	79.01
Z-**1c**	10.80	10.80	6.47	90.00

[a] The length of the unit cell (*a*, *b* or *c*), which is parallel to the axis of the hydrogen-bond column.

The structures were solved by direct methods with SHELXS 86,[11] MULTAN 78[12] or SIR 92,[13] and refined by full-matrix least-squares techniques. All of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were localized from a difference Fourier synthesis, except for *Z*–**1c**. The isotropic thermal parameters of the hydrogen atoms were fixed in the cases of *E*–**9a** and *E*–**10a**, and refined in the other cases. Concerning *E*-**1b**, the phenyl and ethyl groups of the carboxylate were disordered with positional occupancies of 1 : 1. The final *R*-factors and other crystallographic information are summarized in Table 4. Atomic coordinates, thermal

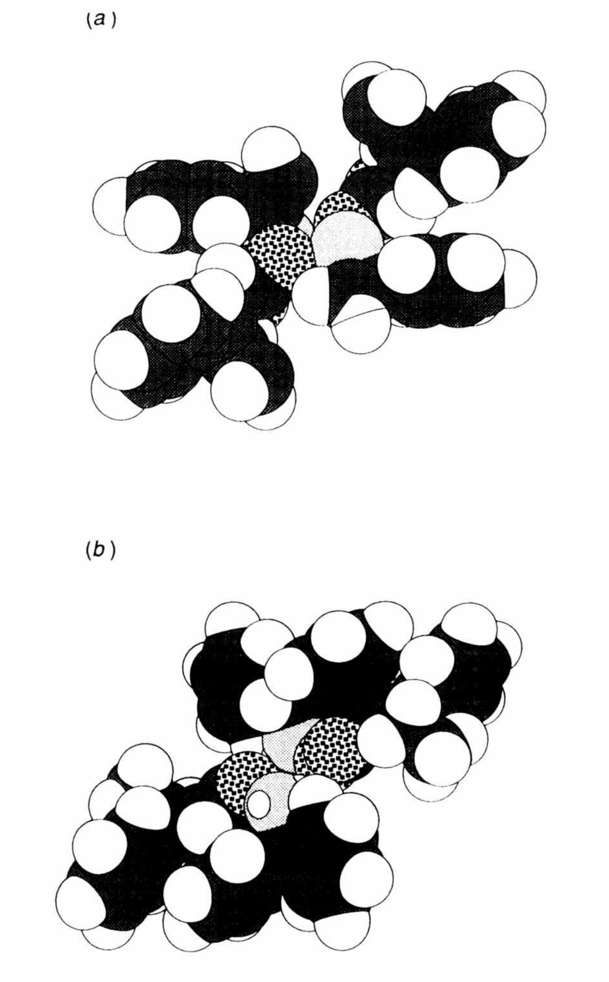

Fig. 9 Space-filling model of the columnar hydrogen-bond network of (*a*) *E*-**1a** and (*b*) *E*-**1d** viewed down the axis of the column

parameters, bond lengths and angles for all salts have been deposited at the Cambridge Crystallographic Data Centre. For details of the deposition scheme, see 'Instruction for Authors '. *J. Chem Soc.*, *Perkin Trans. 2*, 1996, issue 1.

Preparation and solid state reaction of ammonium salts of α,β-unsaturated carboxylic acids

α,β-Unsaturated carboxylic esters were prepared by the Wittig–Horner reaction[14] of the corresponding ketones with ethyl diethylphosphonoacetate (**1**, **7**, **8**, **10**, **11**, **12** and **13**) or the Reformatsky reaction,[15] followed by dehydration (**3** and **4**). The products were mixtures of (*E*)- and (*Z*)-isomers, which were roughly separated by silica-gel column chromatography (eluent: hexane with a trace amount of diethyl ether). The resulting esters were hydrolysed with potassium hydroxide in aqueous ethanol. The crude acids were obtained almost quantitatively and purified by recrystallization.

(*E*)-3-(4-*tert*-butylphenyl)pent-2-enoic acid, *E*-13. Mp 136.0–138.5 °C (Found: C, 77.5; H, 8.8. Calc. for $C_{15}H_{20}O_2$: C, 77.54; H, 8.67%); ν_{max}(KBr)/cm^{-1} 1680, 1600, 1290, 1210, 920, 870 and 830; δ_H($CDCl_3$) 1.10 (3 H, t, *J* 8, CH_3CH_2), 1.33 [9 H, s, $C(CH_3)_3$], 4.12 (2 H, q, *J* 8, CH_3CH_2), 6.07 (1 H, s, olefinic), 7.40 (4 H, s, aromatic) and 10.73 (1 H, br s, COOH).

(*Z*)-3-(4-*tert*-butylphenyl)pent-2-enoic acid, *Z*-13. Mp 114.0–116.0 °C (Found: C, 77.4; H, 8.8. Calc. for $C_{15}H_{20}O_2$: C, 77.54; H, 8.67%); ν_{max}(KBr)/cm^{-1} 1700, 1640, 1270, 1200, 880 and 840; δ_H($CDCl_3$) 1.02 (3 H, t, *J* 8, CH_3CH_2), 1.31 [9 H, s, $C(CH_3)_3$], 2.45 (2 H, q, *J* 8, CH_3CH_2), 5.81 (1 H, s, olefinic), 7.08 (2 H, d, *J* 8, aromatic), 7.32 (2 H, d, *J* 8, aromatic) and 11.10 (1 H, br s, COOH).

Recrystallization of an equimolar mixture of the acid and an amine from ethanol–water or hexane–benzene afforded the ammonium salt almost quantitatively.

Photoreaction of the salts in the solid state. A finely powdered sample (100 mg) was placed in a quartz cell and irradiated with a 500 W super-high-pressure mercury lamp for 24 h at room temperature under an argon atmosphere. After irradiation, the ratio of the (*E*)- and (*Z*)-isomers was determined by ^1H NMR analysis of the irradiated sample.

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