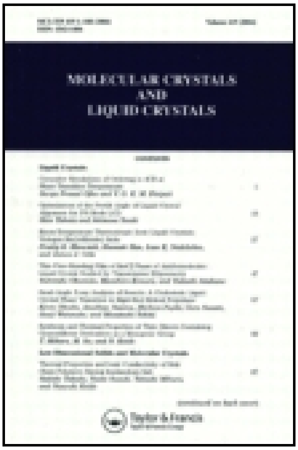

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Crystal and Molecular Structure of Ammonium trans-2-Butenoate, and a Preliminary Investigation of its Solid-State Reactivity

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Version of record first published: 21 Dec 2006

To cite this article: Lin Yang & Bruce M. Foxman (2006): Crystal and Molecular Structure of Ammonium trans-2-Butenoate, and a Preliminary Investigation of its Solid-State Reactivity, Molecular Crystals and Liquid Crystals, 456:1, 25-33

To link to this article: http://dx.doi.org/10.1080/15421400600786280

Mol. Cryst. Liq. Cryst., Vol. 456, pp. 25–33, 2006
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400600786280

Crystal and Molecular Structure of Ammonium *trans*-2-Butenoate, and a Preliminary Investigation of its Solid-State Reactivity

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Ammonium trans-2-butenoate, $NH_4(O_2CCH{=}CHCH_3)$ 5 crystallizes in a similar fashion to metal two-dimensional coordination polymers, and thus is a candidate for facile radiation-induced solid-state reactions. The tetrahedral coordination of the ammonium is an obvious consequence of hydrogen bonding, but the relatively long N···O distance (compared to a Group IA metal) leads to repeat distances along the bilayer of ca. 4.7 Å. Interlayer contacts appear to be suitable for a radiation-induced Michael addition to occur. However, as observed for other nonmetal salts (e.g., those of propynoic acid), the material is stable to γ-ray doses up to 336 kGy.

Keywords: solid-state reactivity; gamma ray; carboxylate

INTRODUCTION

Group Ia or IIa metal salts of *trans*-2-butenoic acid are excellent reactants for solid-state transformations. Heating sodium *trans*-2-butenoate **1** leads to one of two possible diastereomers of disodium 1-hexene-3,4-dicarboxylate **2** [1], while ^{60}Co γ-irradiation of **1** leads to trimer **3** [2], one of eight possible diastereomeric products. Irradiation of the calcium salt leads to cyclodimer **4**, one of four possible diastereomers [3]. In order to extend the range of possible reactions, and to explore the reactivity and potential radical chemistry of the butenoate moiety in the absence of a metal ion, we have

We thank the National Science Foundation (Grant DMR-0504000) for partial support of this research.

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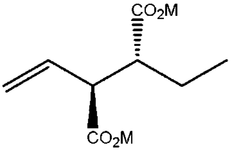
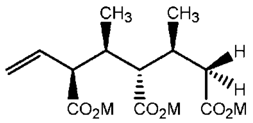
synthesized the simple ammonium salt, $NH_4(O_2CCH{=}CHCH_3)$ **5**, determined its crystal structure, and studied its solid-state reactivity. Here we report the crystal and molecular structure, and discuss aspects of hydrogen bonding, contacts between potentially reactive C atoms and the behavior of **5** upon exposure to ionizing radiation.



2, M = Na



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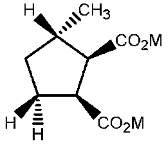


4, M = $Ca_{0.5}$

EXPERIMENTAL SECTION

Instrumentation

NMR spectra were recorded on a Varian XL-400 spectrophotometer. A Gammacell 220 Irradiator (Atomic Energy of Canada Ltd.) equipped with a ^{60}Co source, nominal activity 1.95 kGy d^{-1}, was used for γ-irradiation experiments.

Synthesis of Ammonium *trans*-2-butenoate (5)

Group IA *trans*-2-butenoates and hydrogen di-*trans*-2-butenoates are known [4]. Initial synthetic attempts focused on an analogue of the hydrogen di-*trans*-2-butenoate. Ammonium hydroxide (479.8 mg, 4.0 mmol) was slowly added to a solution of *trans*-2-butenoic acid (702.8 mg, 8.0 mmol) in 20 mL of ethanol. The solution was stirred for 2 h and filtered. Slow evaporation of the solvent yielded crystalline material, but vapor diffusion gave the best results. An aliquot of the filtrate (2.5 mL) was transferred to a 45 × 15 mm vial, which was placed in a disposable scintillation vial (20 mL) containing ether (10 mL). The disposable scintillation vial was capped and placed in the refrigerator (5°C). After 2 d, large prismatic crystals of **5** formed. An X-ray structure determination (*vide infra*) showed that the material was ammonium *trans*-2-butenoate, rather than ammonium hydrogen di-*trans*-2-butenoate [4], despite the 2:1 ratio of reagents. Even when a 4:1 ratio of acid:base was used in an separate experiment, the results were identical. It was thus not possible to synthesize the ammonium hydrogen di-*trans*-2-butenoate salt [4]. The simple salt **5** is a colorless solid, m.p. 84°C; the experimental density, measured by neutral buoyancy in cyclohexane/$CHCl_3$, was 1.14(1) g·cm^{-3}. ^{1}H NMR:

δ 1.83 (dd, 3, $J = 1.8$, 6.8), 5.86 (dq, 1, $J = 1.3$, 15.3), 6.84 (dq, 1, $J = 6.7$, 15.3); ^{13}C NMR δ 17.8, 125.3, 144.3, 174.8.

Irradiation of 5

Crystals of **5** (200 mg) were placed in a 3 mm i.d. glass tube and packed tightly using a glass rod. A septum was placed at the top of the glass tube and the sample evacuated for 3 min. The sample was then placed under nitrogen for 3 min and sealed using an air/gas flame. While irradiation of **5** led to a light yellow coloration, ^{1}H NMR analysis of aliquots showed no obvious new peaks after 103 kGy γ-irradiation, and only tiny broad peaks (1–3 ppm) after a 336 kGy dose. NMR analysis thus indicated that no significant product formed under these conditions.

Collection of X-ray Diffraction Data and Structure Determination

A single crystal of **5** was selected, mounted on a Pyrex fiber affixed to a brass pin, and optically centered on an Enraf-Nonius CAD4-U diffractometer equipped with CuKα radiation. X-ray data were collected using the Enraf-Nonius EXPRESS program [5]. The structure was solved by direct methods using SIR-92 [6] and refined using the Oxford *CRYSTALS for Windows* [7,8] package. Non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms were located on an electron density difference map and refined using isotropic displacement parameters. Pertinent details of the structure determination appear in Table 1. CCDC 285595 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

RESULTS AND DISCUSSION

Crystal Structure and Packing Arrangement of Ammonium *trans*-2-Butenoate

The numbering scheme and asymmetric unit of **5** is depicted in Figure 1. The coordination of the tetrahedral ammonium ion is shown in Figure 2. The ammonium ion is surrounded by four hydrogen-bonded oxygen atoms (Table 2); each oxygen atom arises from a butenoate moiety in a different asymmetric unit. Each oxygen atom in turn is a hydrogen bond acceptor from two ammonium ions, in both a *syn*- and *anti*-fashion.

TABLE 1 Crystallographic Data for $NH_4(O_2CCH{=}CHCH_3)$ (**5**)

Compound	**5**
Chemical Formula	C_4H_9O2N
a, Å	11.0022 (19)
b, Å	6.9070 (7)
c, Å	8.1409 (10)
β, deg.	105.641 (12)
V, $Å^3$	595.74 (14)
Z	4
Formula Wt. g/mol	103.12
Space Group	$P2_1/c$
T, °C	21 (1)
λ, Å	1.54178
ρ_{calc}, $g\,cm^{-3}$	1.150
ρ_{obs}, $g\,cm^{-3}$	1.14 (1)
μ, cm^{-1}	0.770
Transmission factors	0.80–0.85
$\boldsymbol{R}^{a}$	0.0622
$\boldsymbol{R_w}^{b}$	0.0570
$\boldsymbol{S}^{c}$	0.92
no. reflections	1040
no. parameters	101
Secondary extinction	109 (9)

$$^{a}\boldsymbol{R} = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$^{b}\boldsymbol{R_w} = \left[\sum_{w} (|F_o| - |F_c|)^2 / \sum_{w} |F_o|^2\right]^{\frac{1}{2}}$$

$$^{c}\boldsymbol{S} = \left[\sum_{w} (|F_o| - |F_c|)^2 / (n - m)\right]^{\frac{1}{2}}$$

As shown in Figure 3, compound **5** crystallizes in a bilayer structure [9] with alternating hydrogen-bonded and hydrophobic layers parallel to the *bc* plane. The four-coordinate, H-bonded ammonium ion, and the consequent bridging nature of the carboxylate groups mimic a two-dimensional metal coordination polymer, and provide an opportunity for close-packing of the organic tails of the butenoates [9]. However, the relatively long N···N separation of 4.74 Å along the bilayer reduces the chances that this arrangement will lead to C···C contacts of $<$4.2 Å [10].

Solid-State Reactivity of 5

Let us consider the mechanism proposed for the formation of calcium *cis, trans*-nepetate **4** [3]. The scheme shows a plausible mechanism

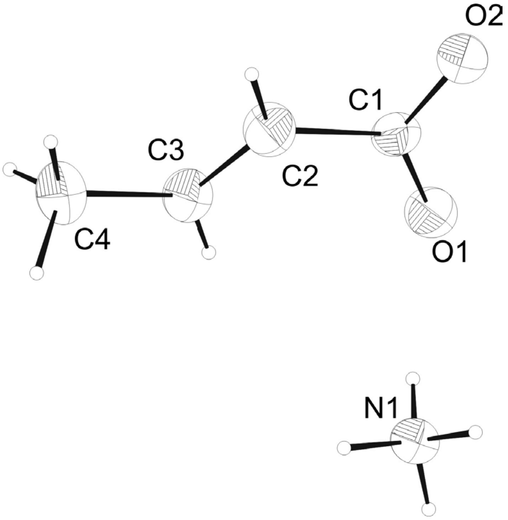


FIGURE 1 Numbering scheme and molecular structure for compound **5**.

for the formation of **4**. γ-Ray induced loss of a hydrogen atom from a *trans*-2-butenoate anion **6** gives radical **A**. Intermolecular addition of **A** to the β-carbon atom of an adjacent butenoate gives radical **B**, which

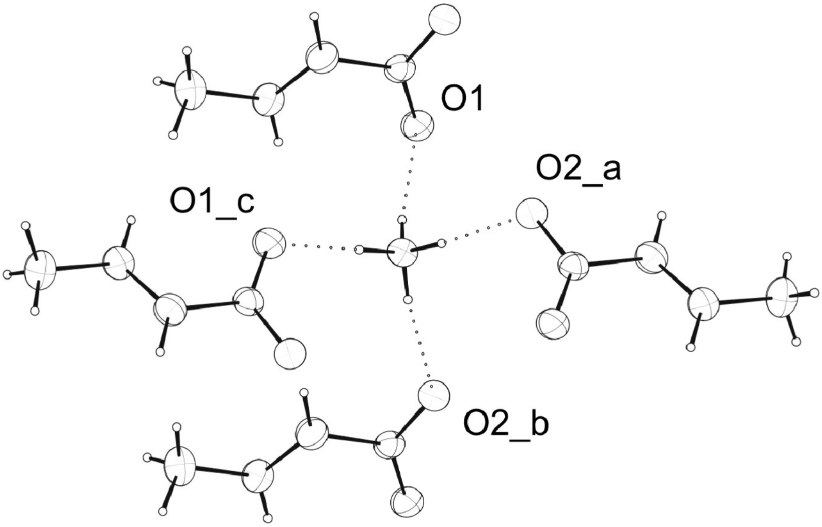
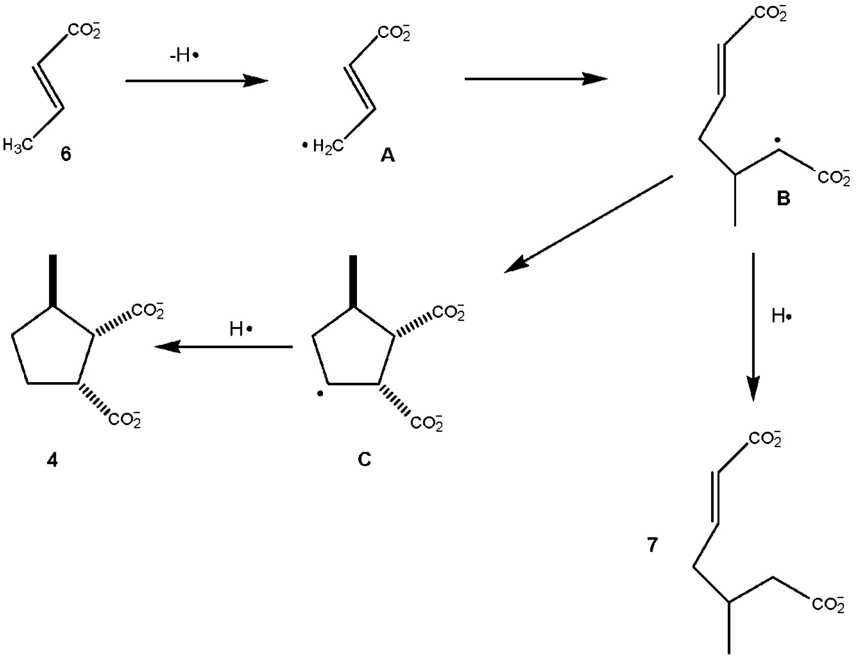


FIGURE 2 Coordination environment of a single ammonium ion in **5**.

TABLE 2 Hydrogen Bond Parameters in Compound **5**

Bond type	D$\cdots$H (Å)	H$\cdots$A (Å)	D$\cdots$A (Å)	Angle (°)	Symmetry opn (abbrev)
N1–H1$\cdots$O1	0.88 (2)	2.01 (2)	2.861 (1)	161 (2)	
N1–H2$\cdots$O2	0.92 (2)	1.90 (2)	2.802 (1)	167 (2)	$-x$, $1/2+y$, $3/2-z$ (_a)
N1–H3$\cdots$O2	0.92 (2)	1.93 (2)	2.835 (1)	172 (2)	x, $1+y$, z (_b)
N1–H4$\cdots$O1	0.93 (2)	1.89 (2)	2.814 (2)	177 (2)	x, $1/2-y$, $1/2+z$ (_c)

could undergo a rare, but precedented [11], 5-*endo* cyclization to give cyclopentyl radical **C** which could abstract a hydrogen atom from another molecule of **6** to generate **4**. Hydrogen abstraction by radical **B** would give 5-methyl-2-heptenedioic acid (**7**) [3].



For the nepetate cyclodimerization reaction to occur, C4$\cdots$C3′ and C2$\cdots$C2′ distances less than ca. 4.2 Å between the same molecule should be present in the crystal structure [10]. In the present case, however, the nearest approaches are C4$\cdots$C3′, 4.78 Å and C2$\cdots$C2′, 4.67 Å, related by the symmetry operation $(x, -1/2-y, 1/2+z)$. To

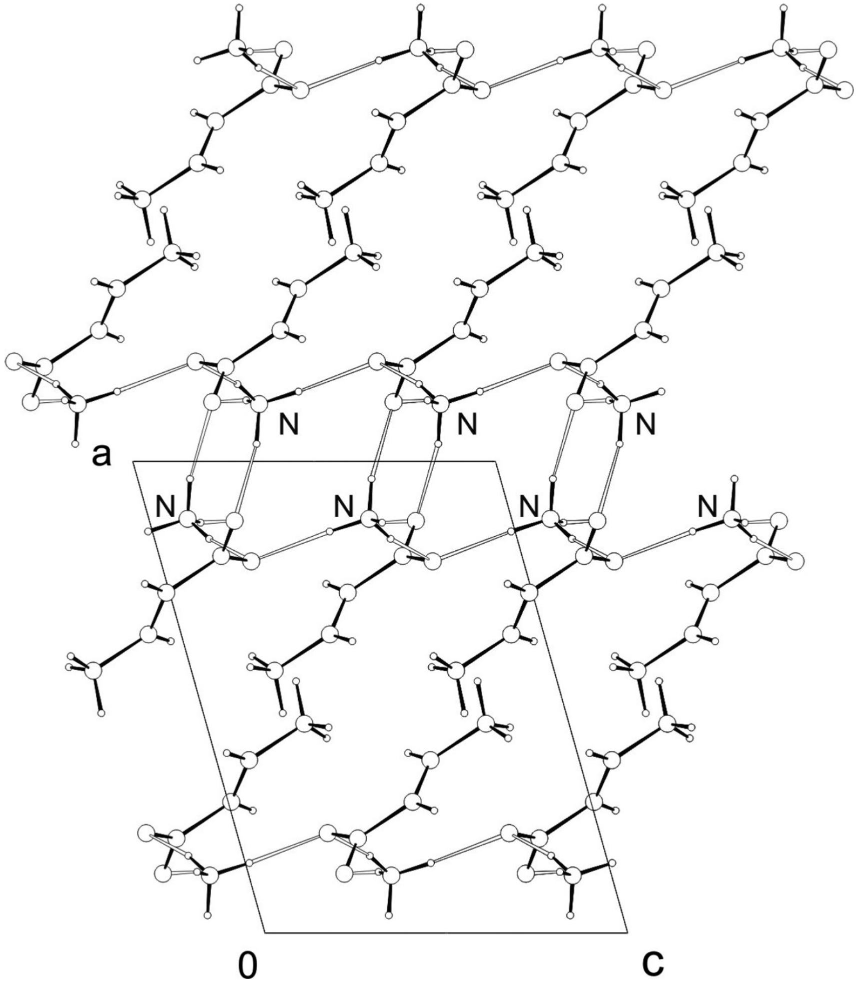


FIGURE 3 View of **5** along *b* axis, showing the bilayer arrangement of the structure.

complete the analysis, we consider the distances associated with the possible formation of Michael addition product **7**. A chain process could be initiated by loss of a hydrogen atom from a butenoate as above, followed by attack of the resultant allyl radical on the β-carbon atom of the parent butenoate [C4$(1-x, 1/2+y, 5/2-z)\cdots$C3, 3.903 Å]; the process will be completed, along with the generation of a new allyl radical to ensure chain propagation, by abstraction of an H atom by C2 of the parent butenoate [C2$\cdots$H41$(x, -1/2-y, z-1/2)$].

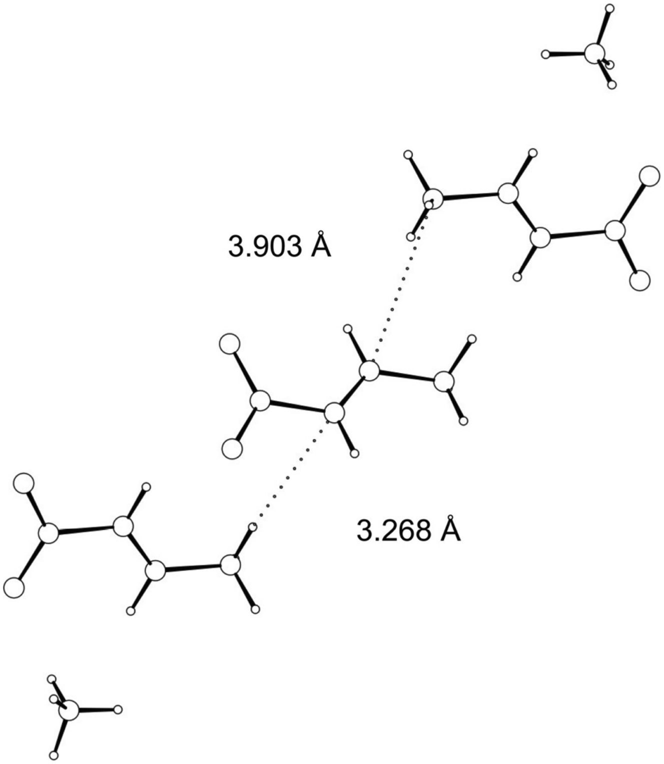


FIGURE 4 Short contacts (Å) and possible addition/abstraction course for a putative solid-state Michael addition.

A partial view of the chain is shown in Figure 4. However, NMR analysis on the sample of γ-irradiated **5** showed that no significant amount of product formed after a 336 kGy dose. This observation is consistent with the lack of reactivity observed for organic derivatives of unsaturated species such as priopiolaldehyde semicarbazone [12], 4-(1-pyrrolidino)-pyridinium propynoate [13] or 2-aminopyridinium propynoate [14]. However, further work, e.g., a very high radiation dose an order of magnitude greater than available with the irradiator at Brandeis University, is required to pursue this objective.

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