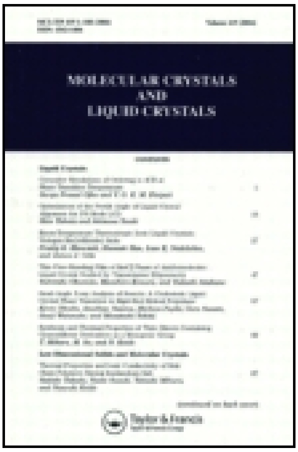

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The Structure and Solid State Reactivity of a Cocrystal of Propynoic Acid and 4-(1 -pyrrolidino)-pyridine. A Study of γ-Ray-Induced vs. Thermal Reactivity

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THE STRUCTURE AND SOLID STATE REACTIVITY OF A COCRYSTAL OF PROPYNOIC ACID AND 4-(1-PYRROLIDINO)-PYRIDINE. A STUDY OF γ-RAY-INDUCED VS. THERMAL REACTIVITY.

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(*Received September 12, 1991*)

Abstract Mixing propynoic acid and 4-(1-pyrrolidino)-pyridine in ethanol produces the salt 4-(1-pyrrolidino)-pyridinium propynoate (**1**) in high yield. An X-ray structure determination of **1** (Space Group $P2_1$, Z = 4) shows it to contain two independent cation-anion sets. Each set is interconnected by N-H···O and C-H···O hydrogen bonds; there are no hydrogen bonds formed between the two sets. Each set contains an infinite array of short acetylene-acetylene contacts (3.57 and 3.74 Å, respectively); despite this characteristic, the material does not polymerize upon exposure to ^{60}Co γ-rays. Heating **1** at 125 °C for 23 hours converts it, in high yield, to a 19:1 mixture of (*E* and *Z*)-4-(1-pyrrolidino)-pyridinium-1-acrylate. To the best of our knowledge, this is the first example of the addition of a pyridine moiety to an acetylene in the solid state.

Keywords: solid-state reaction, cocrystal, michael addition, acrylate, pseudosymmetry, structure determination

INTRODUCTION

Upon irradiation with ^{60}Co γ-rays, metal propynoates are readily converted to mixtures of acetylenic oligomers.[1-4] The information available to date[2-4] suggests that the most important factors which influence this reaction include: (a) distance (less than ≈ 4.2 Å for acetylene - acetylene contacts, with inter-acetylene angles of little importance); (b) lattice energy of the reactant (for isomorphous series, those with greater lattice energy are *less* reactive); and (c) the absorption cross-section of the material for γ-rays (generally, propynoate salts of heavier metals are more reactive). In separate experiments we[5,6] and others[7] have observed that solid organic acetylenes are *considerably* less reactive than the metal-containing species. However, owing to the lack of available information, we must make this comparison between the salts of an acetylenic carboxylic acid and organic derivatives such as amides and semicarbazones. Certainly, a more appropriate comparison could be offered if an *analogous* organic derivative became available. Ideally, such a crystalline derivative would have short -C≡C·····C≡C- contacts between *anionic* propynoates. Our initial attempts thus focused on the preparation of simple amine salts of propynoic acid. While the preparation of such materials was straightforward, single crystals of the products could not be grown. Etter[8] has demonstrated that cocrystals of carboxylic acids with planar amine/pyridine systems lead to interesting, highly crystalline materials containing strong hydrogen bonds. For one of these, the 1:1 cocrystal of 2-aminopyrimidine with succinic acid, a relatively short unit cell translation, 5.045 Å, was observed.[8] This suggested to us that a study of cocrystals between propynoic acid and planar amine/pyridine moieties might produce materials with short contacts between acetylene moieties. While the acceptor, 4-(1-pyrrolidino)-pyridine, contains only a single acceptor atom, it seemed likely that the packing might be controlled by the planar nature of the acceptor. This paper reports the crystal structure of cocrystals formed between propynoic acid and 4-(1-pyrrolidino)-pyridine, as well as their behavior upon heating and exposure to γ-rays.

EXPERIMENTAL SECTION

Instrumentation

Melting points were determined on a Laboratory Devices Mel-Temp apparatus and are uncorrected. IR spectra were recorded using Mattson Cygnus 100 FT-IR and Perkin-Elmer 683 spectrophotometers. ^{1}H and ^{13}C NMR spectra were recorded on Varian EM-390 (90 MHz) and XL-300 (300 MHz) spectrometers. Chemical shifts are given in parts per million downfield from 3-(trimethylsilyl)-1-propane sulfonic acid sodium salt. The following abbreviations are used to indicate signal multiplicity (NMR) or spectral characteristics (IR): s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; b, broad; sh, shoulder. A Gammacell 220 Irradiator (Atomic Energy of Canada, Ltd.) equipped with a ^{60}Co source was used for all γ-irradiation experiments. The nominal activity of the source as of 1 July 1991 was 0.043 Mrad/h.

4-(1-Pyrrolidino)-pyridinium Propynoate (1)

To 0.200 g (2.86 mmol) of propynoic acid in 15 mL of EtOH was added 4-(1-pyrrolidino)-

pyridine (0.423 g, 2.89 mmol) at 25 °C. The solution was stirred for 30 min forming a clear-brown homogeneous solution. The solution was filtered over Celite and evaporated under reduced pressure (25 torr) to give **1** (0.598 g, 2.74 mmol, 96.2%) as a tan solid: IR (KBr) 3285 (sh), 3215, 3180 (sh), 3050, 2977, 2931, 2876, 2082, 1644, 1586 cm^{-1}; ^{1}H NMR (D_2O) δ 7.98 (1 H, d, *J* = 7.6 Hz), 6.74 (1 H, d, 7.6 Hz), 3.50 (2 H, m), 3.09 (1 H, s), 2.10 (2 H, m); ^{13}C NMR (D_2O) δ 180.1 (C), 157.4 (C), 140.8 (CH), 110.1 (CH), 73.2 (CH), 50.9 (CH_2), 27.42 (CH_2), one (C) carbon not observed. Solid **1** was irradiated with ^{60}Co γ-rays (61 Mrad); the ^{1}H NMR spectrum of the colorless irradiated material was identical to the spectrum of the starting material.

(*E* and *Z*)-4-(1-Pyrrolidino)-pyridinium-1-acrylate (2 and 3)

At 760 torr, 99 mg (0.45 mmol) of crystalline solid **1** was heated at 90 °C for 6.25 h. The resulting dark brown material (97 mg) gave a 95:5 mixture of *E* (**2**) and *Z* (**3**) pyridinium salts in 23% combined yield estimated from integration of ^{1}H NMR spectra. Other experiments gave identical product distribution: at 90 °C, heating for 23.5 h led to 73% conversion; at 125 °C, heating for 2, 7 and 23 h led to conversions of 28, 83 and >90%, respectively.

2: mp 230-232 °C; IR 3060, 2960, 2870, 1680, 960 cm^{-1}; ^{1}H NMR (D_2O) δ 8.16 (1 H, d, *J* = 7.9 Hz), 7.53 (1 H, d, *J* = 14.2 Hz), 6.83 (1 H, d, 7.9 Hz), 6.29 (1 H, d, *J* = 14.2 Hz), 3.61 (2 H, m), 2.10 (2 H, m); ^{13}C NMR (D_2O) δ 175.2 (C), 157.0 (C), 142.0 (CH), 141.2 (CH), 119.5 (CH), 111.2 (CH), 51.8 (CH_2), 27.4 (CH_2).

3: ^{1}H NMR (D_2O) δ 8.16 (1 H, d, *J* = 7.9 Hz), 6.90 (1 H, d, *J* = 9.1 Hz), 6.83 (1 H, d, 7.9 Hz), 6.14 (1 H, d, *J* = 9.1 Hz), 3.62 (2 H, m), 2.10 (2 H, m); ^{13}C NMR (D_2O) δ 156.4 (C), 141.0 (CH), 133.4 (CH), 126.0 (CH), 110.3 (CH), 51.4 (CH_2), 27.4 (CH_2), one (C) carbon not observed.

Structure Determination of 1

Single crystals were grown by slow evaporation from hexanes. Lauê photographs and a preliminary X-ray photographic study indicated the crystal to be of excellent quality. The crystal was then transferred to a Supper No. 455 goniometer and optically centered on a Syntex $P2_1$ diffractometer. Operations were performed as described previously.[9] The analytical scattering factors of Cromer and Waber were used; real and imaginary components of anomalous scattering were included in the calculations.[10] The structure was solved using SHELXS-86;[11] all other computational work was carried out on a VAX 6420 computer using the Enraf-Nonius SDP software package.[12] At the conclusion of least-squares refinement of positional and anisotropic displacement parameters for all nonhydrogen atoms (isotropic displacement parameters for H atoms attached to N; H atoms attached to C included as fixed contributions to F_c, with $B_H = 1.3 \cdot B_{eq}$ of attached C atom), R = 0.048 and R_w = 0.055. Two separate least-squares refinements of the structure (hereafter designated refinements *A* and *B*), carried out by each author independently, resulted in *convergence*, with R values ≈ 0.048 and 0.059. The parameters obtained were significantly but not greatly different. This appears to be the result of an unusual pseudosymmetry, leading to a false minimum in the refinement (as it turned out, this occurred only for refinement *B*). While the two independent anions are *not* simply related to one another, the cations are related by the pseudo-translation ≈ (0.5, 0.37, 0.68). This leads to a considerable number of translation-related absences and reflections of low intensity in the diffraction pattern. The two refinements became equivalent when *all* data were used in *A* and *B*, together with the application of unit weights in the refinement of these data.[13] Model *A* changed little, while the parameters of *B* shifted from the false minimum to become identical with those of *A*. The final refinement was carried out in the usual manner, using only those data for which $I > 1.96\ \sigma(I)$. The data above and in the Tables and Figures correspond to that refinement. The results were not significantly different from those obtained in *A*. Complete experimental detail is presented in Table I, atomic coordinates in Table II, and bond lengths and angles in Table III. Tables of anisotropic displacement parameters, calculated H atom coordinates, and observed and calculated structure amplitudes are available from the authors.

Table I

Data for the X-ray Diffraction Study of $[C_9H_{13}N_2]^+[C_3HO_2]^-$

(A) Crystal Data at 21(1)°C.

Crystal system: Monoclinic
Space group: $P2_1$ [C_2^2; No. 4]
$a = 15.525(5)$ Å
$b = 7.177(3)$ Å
$c = 10.430(4)$ Å
$\beta = 96.21(4)°$
$V = 1155.3$ Å^3

$Z = 4$
Crystal Size: 0.63 x 0.50 x 0.29 mm.
Formula Wt : 218.26
$\rho_{calc} = 1.255$ g-cm^{-3}
$\rho_{obs} = 1.25(2)^a$ g-cm^{-3}
$\mu = 0.812$ cm^{-1} (MoKα)

Cell constant determination : 7 pairs of ± (hkl) and refined 2θ, ω, χ values in the range $25 \leq |2\theta| \leq 27°$ (λ(MoKα) = 0.71073Å)

(B) Measurement of Intensity Data

Radiation : MoKα, graphite monochromator
Reflections measured : $+h$, $+k$, $\pm l$ ($3 \leq 2\theta \leq 50°$)
Scan type, speed : θ-2θ, vble, 2.93 - 5.33°/min
Scan range : symmetrical, $[1.90 + \Delta(\alpha_2-\alpha_1)]°$
No. of reflections measured : 2312, 2228 in unique set
Standard reflections, period 74: 921, 10 0 0, 126 ; variation $\leq \pm 3\sigma(I)$ for each
Absorption correction : empirical, normalized transmission factors 0.899 - 1.000, 130, 140, 240
Data reduction: as before[b]
Statistical information : $R_{av} = 0.016$ (*0kl* reflections)

(C) Refinement

Refinement[c], with 1666 data for which $I > 1.96\ \sigma(I)$
Weighting of reflections : as before[c], p = 0.04
Solution : SHELXS-86,[11] difference-Fourier
Refinement[d] : full-matrix least-squares, with:
  anisotropic displacement parameters for C, N, and O atoms;
  isotropic displacement parameters for H atoms;
  secondary extinction parameter, $9.08(5) \times 10^{-7}$;
  $R = 0.048$; $R_w = 0.055$; SDU = 1.899;
  R (structure factor calcn with all 2228 reflections) = 0.079
Final difference map : random peaks ranging from -0.161 to +0.181e/Å^3.

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[a] Measured by neutral buoyancy in *n*-hexane/1,1-dibromomethane.

[b] Foxman,B.M.;Goldberg,P.L.;Mazurek,H. *Inorg.Chem.* **1981**, 20, 4381; all computations in the present work were carried out using the ENRAF-NONIUS Structure Determination Package.[12]

[c] Corfield,P.W.R.; Doedens,R.J.; Ibers,J.A. *Inorg.Chem.* **1967**, 6, 197.

[d] $R_{av} = \Sigma|I-I_{av}|/\Sigma I$; $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $R_w = \{\Sigma w[|F_o|-|F_c|]^2/\Sigma w|F_o|^2\}^{1/2}$
SDU = $\{\Sigma w[|F_o|-|F_c|]^2/(m-n)\}^{1/2}$ where m (=1666) is the number of observations and n (=298) is the number of parameters.

Table II. Atomic Coordinates for $[C_9H_{13}N_2]^+[C_3HO_2]^{-a,b}$

Atom	x	y	z	B(Å^2)
O1	0.8342(1)	0.0479(5)	0.5185(2)	6.38(6)
O2	0.8072(2)	-0.0339(5)	0.3134(2)	7.00(8)
N1	0.6445(2)	0.0426(5)	0.3619(3)	5.11(7)
N2	0.3867(2)	0.0478(5)	0.4124(2)	4.52(6)
C1	0.8541(2)	-0.0203(6)	0.4181(3)	5.04(9)
C2	0.9414(2)	-0.1022(7)	0.4181(3)	5.34(9)
C3	1.0105(3)	-0.1698(8)	0.4209(4)	7.1(1)
C4	0.5853(2)	0.0409(7)	0.2600(3)	5.42(9)
C5	0.4991(2)	0.0468(7)	0.2731(3)	5.33(9)
C6	0.4707(2)	0.0507(6)	0.3978(3)	4.10(7)
C7	0.5358(2)	0.0576(6)	0.5027(3)	4.24(7)
C8	0.6204(2)	0.0512(6)	0.4820(3)	4.71(8)
C9	0.3521(2)	0.0505(7)	0.5366(3)	5.01(8)
C10	0.2558(2)	0.045(1)	0.5006(4)	9.2(1)
C11	0.2382(3)	0.023(1)	0.3707(4)	11.5(2)
C12	0.3177(2)	0.0333(8)	0.3056(3)	6.0(1)
HN1	0.705(2)	0.036(7)	0.355(3)	8(1)
O3	1.3350(2)	0.5379(6)	0.2165(2)	7.89(8)
O4	1.3296(1)	0.4054(5)	0.0256(2)	6.22(6)
N3	1.1588(2)	0.4169(5)	0.0563(3)	4.99(6)
N4	0.8972(2)	0.4216(5)	0.0859(2)	4.38(6)
C13	1.3663(2)	0.4946(6)	0.1169(3)	4.95(9)
C14	1.4544(2)	0.5613(8)	0.1027(3)	5.73(9)
C15	1.5220(2)	0.6243(8)	0.0861(4)	7.1(1)
C16	1.1300(2)	0.4288(6)	0.1725(3)	5.06(8)
C17	1.0446(2)	0.4300(6)	0.1864(3)	4.83(8)
C18	0.9826(2)	0.4200(5)	0.0767(3)	3.96(7)
C19	1.0160(2)	0.4131(6)	-0.0443(3)	4.43(7)
C20	1.1020(2)	0.4109(6)	-0.0507(3)	4.91(8)
C21	0.8588(2)	0.4323(8)	0.2094(3)	6.3(1)
C22	0.7640(3)	0.439(2)	0.1647(4)	13.2(3)
C23	0.7480(3)	0.401(1)	0.0382(4)	8.9(1)
C24	0.8305(2)	0.4156(7)	-0.0239(3)	5.13(8)
HN3	1.223(2)	0.402(6)	0.055(3)	7.0(9)

[a] Atoms refined using anisotropic displacement parameters are given in the form of the isotropic equivalent displacement parameter defined as:

$$1.33\cdot[a^2\cdot B_{11} + b^2\cdot B_{22} + c^2\cdot B_{33} + ab\cdot\cos\gamma\cdot B_{12} + ac\cdot\cos\beta\cdot B_{13} + + bc\cdot\cos\alpha\cdot B_{23}]$$

[b] Numbers in parentheses in this and following tables are estimated standard deviations in the least significant digit.

Table III. Bond Lengths (Å) and Angles (°) for $[C_9H_{13}N_2]^+[C_3HO_2]^-$

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
O1	C1	1.226(4)	O3	C13	1.233(4)
O2	C1	1.249(4)	O4	C13	1.235(4)
N1	C4	1.329(4)	N3	C16	1.339(4)
N1	C8	1.346(4)	N3	C20	1.346(4)
N2	C6	1.329(4)	N4	C18	1.339(4)
N2	C9	1.455(4)	N4	C21	1.479(4)
N2	C12	1.464(4)	N4	C24	1.459(4)
C1	C2	1.478(5)	C13	C14	1.472(5)
C2	C3	1.175(6)	C14	C15	1.172(6)
C4	C5	1.361(5)	C16	C17	1.350(5)
C5	C6	1.418(4)	C17	C18	1.415(4)
C6	C7	1.408(4)	C18	C19	1.416(4)
C7	C8	1.355(4)	C19	C20	1.344(5)
C9	C10	1.501(5)	C21	C22	1.496(5)
C10	C11	1.362(6)	C22	C23	1.343(7)
C11	C12	1.474(6)	C23	C24	1.501(5)

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
C4	N1	C8	120.5(3)	C16	N3	C20	120.0(3)
C6	N2	C9	124.3(2)	C18	N4	C21	123.9(2)
C6	N2	C12	124.1(3)	C18	N4	C24	124.6(3)
C9	N2	C12	111.6(2)	C21	N4	C24	111.5(2)
O1	C1	O2	126.9(3)	O3	C13	O4	126.1(3)
O1	C1	C2	118.4(3)	O3	C13	C14	117.3(3)
O2	C1	C2	114.7(3)	O4	C13	C14	116.6(3)
C1	C2	C3	178.2(4)	C13	C14	C15	175.3(5)
N1	C4	C5	121.5(3)	N3	C16	C17	121.7(3)
C4	C5	C6	120.0(3)	C16	C17	C18	120.2(3)
N2	C6	C5	120.7(3)	N4	C18	C17	122.3(3)
N2	C6	C7	122.9(3)	N4	C18	C19	121.7(3)
C5	C6	C7	116.4(3)	C17	C18	C19	116.1(3)
C6	C7	C8	120.1(3)	C18	C19	C20	120.4(3)
N1	C8	C7	121.4(3)	N3	C20	C19	121.6(3)
N2	C9	C10	103.3(3)	N4	C21	C22	101.9(3)
C9	C10	C11	109.9(3)	C21	C22	C23	111.8(4)
C10	C11	C12	111.3(3)	C22	C23	C24	109.5(4)
N2	C12	C11	103.5(3)	N4	C24	C23	103.3(3)

RESULTS AND DISCUSSION

A view of the two independent molecules, together with the labelling scheme, is shown in Figure 1; the strong N-H···O hydrogen bonds are clearly evident. As expected, the proton has been transferred from propynoic acid (pK_a 1.84) to the pyridine N atom. Consideration of the bond lengths and angles (Table III) suggests that the pyridone-iminium resonance form **4** contributes strongly to the structure of the cation. Distances and angles closely parallel those of the 4-dimethylaminopyridinium cation,[14] for which a structure analogous to **4** is appropriate. While the structure of neutral 4-dimethylaminopyridine[15] is also consistent with a strong contribution from a resonance form analogous to **4**, an analysis of distances in the cation[14] suggests a further shift toward form **4**. Other bond lengths and angles lie within normal ranges.

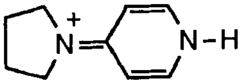

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Figure 2 depicts the N-H···O and C-H···O hydrogen bonding present in the structure, and reveals the reason for the inequivalence of the two propynoate moieties. As the Figure shows, one propynoate anion forms an infinite chain of hydrogen bonds involving both O1(*anti*) and O2(*syn*), while the other propynoate anion is involved in an infinite chain of hydrogen bonds involving only O4 in both a *syn*- and an *anti*-fashion. Table IV presents the hydrogen bond distances and angles for the strong N-H···O and weaker C-H···O interactions. The IR spectrum of solid **1** exhibits an absorption at 3215 cm^{-1}, with shoulders at 3180 and 3285 cm^{-1}. These features are consistent[16] with the C3···O1 distance of 3.16 Å and C15···O4 distance of 3.36 Å.

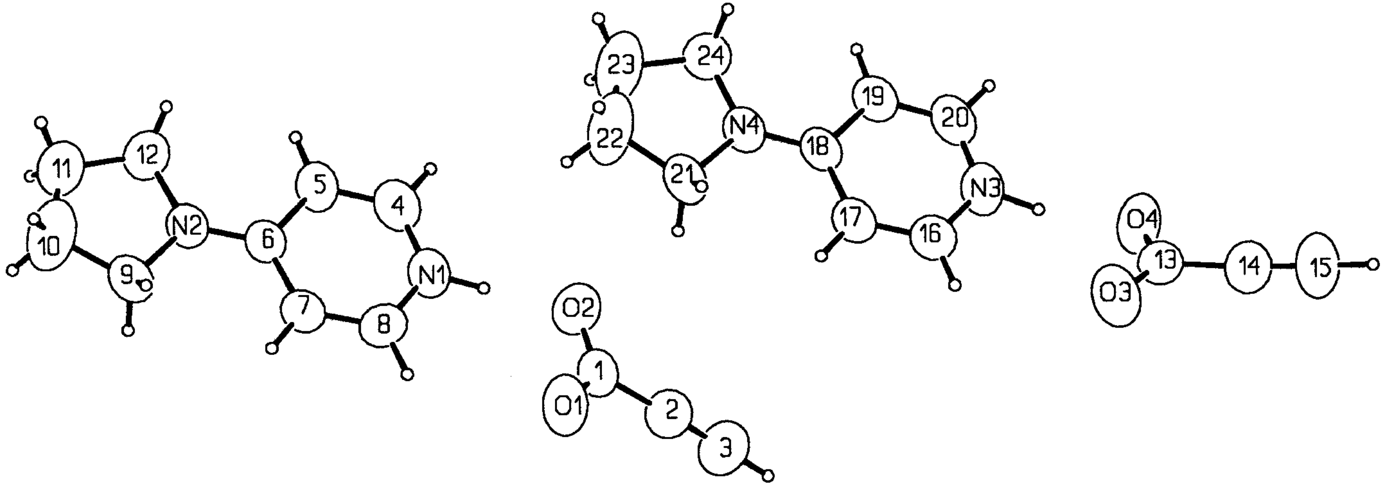


Figure 1. View of the two independent molecules of $[C_9H_{13}N_2]^+[C_3HO_2]^-$, showing the atomic labelling scheme.

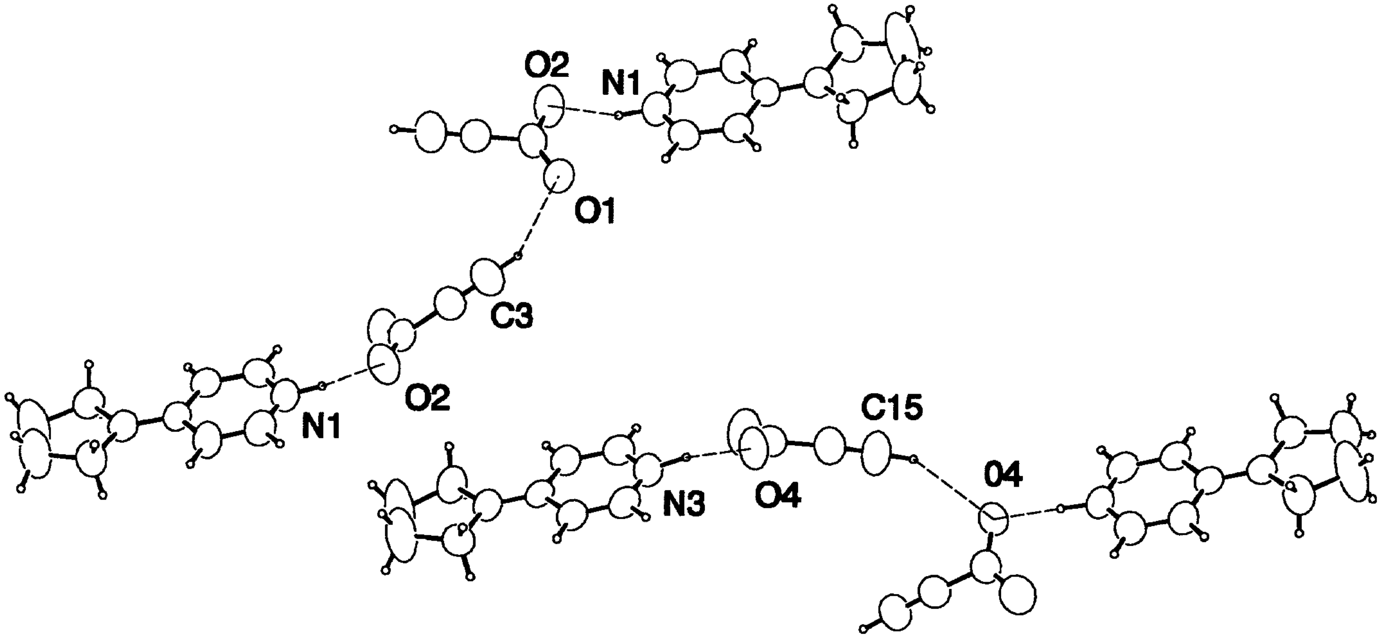


Figure 2. View of the two independent networks of hydrogen bonding in $[C_9H_{13}N_2]^+[C_3HO_2]^-$.

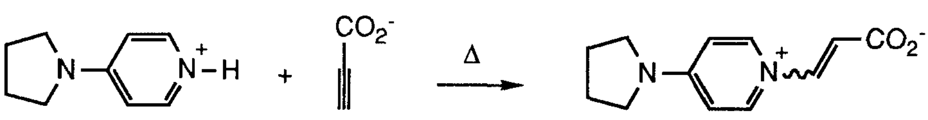
Table IV

X-H···Y	X···Y, Å	X-H···Y, °	Symmetry Operation
N1-HN1···O2	2.685	162.5	*x, y, z*
N3-HN3···O4	2.706	168.6	*x, y, z*
C3-H3····O1	3.160	153.0	*2 - x, y - 1/2, 1 - z*
C15-H15··O4	3.364	152.6	*3 - x, 1/2 + y, z̄*

The repetitive series of short C2-C3' [*2 - x, 1/2 + y, 1 - z*] contacts (3.569 Å) is shown in Figure 3. An analogous set of 3.742 Å contacts, not depicted here, occur between the α and β' acetylenic carbon atoms C14-C15' [*3 - x, y - 1/2, z̄*]. In metal propynoates, such arrangements characterize the material as a phase which will readily undergo solid state polymerization in the presence of X- or γ-rays.[2-4] However, 4-pyrrolidinopyridinium propynoate (**1**) is stable under conditions which lead to high levels of conversion for the corresponding metal propynoates. This points once again to the special role of metals in effecting the solid state reactivity of the propynoate moiety. The present result indicates that increasing the ionic character of the crystal lattice is *not* an important influence on the reactivity of the propynoate moiety.

Thermally-induced solid state reactivity of **1**.

Heating solid **1** at temperatures ≥ 90 °C converts it, in high yield, to the *E* and *Z* isomers of 4-(1-pyrrolidino)-pyridinium-1-acrylate (**2** and **3**), respectively. While increasing the temperature



1

2 - *E* 95%
3 - *Z* 5%

decreases the time required for conversion, it does not affect the ratio of *E*:*Z* isomers, which remains constant at 19:1 over time and a temperature range of 90 - 125 °C.

Michael additions of substituted pyridines to acetylenes are readily carried out in solution;[17]

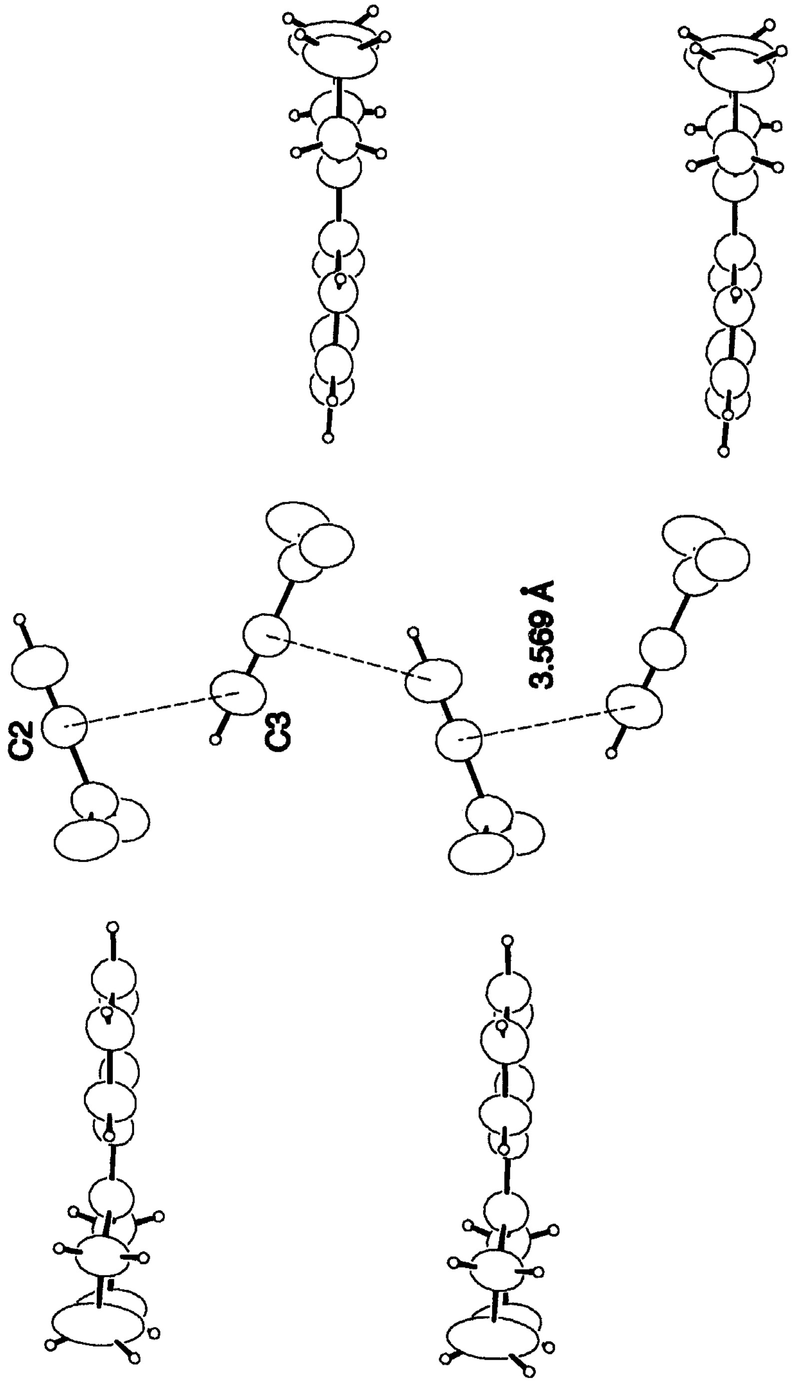


Figure 3. View of one of the two repeating chains of short acetylene - acetylene contacts in $[C_9H_{13}N_2]^+[C_3HO_2]^-$.

the predominance of the *E* isomer is consistent with that observed for similar reactions in solution.[18] However, to the best of our knowledge, such additions have not been previously observed in the solid state. The availability of structural data provides an opportunity to obtain information regarding the geometrical course of a reaction and/or the structural criteria for the onset of a solid state reaction. Inspection of the intermolecular contacts for **1** revealed only one N-C contact < 5.4 Å (N1-C15 [*x*, *y* - *1*, *z*], 4.44 Å). Thus it seemed likely that there *might* be an intermediate phase formed at higher temperatures. It would follow that this phase would contain pairs of anions and cations in a suitable orientation for reaction to occur. We heated **1** at 90 °C for 1 h; after that time, X-ray powder photographic studies revealed that a new phase had formed. The diffraction pattern was quite different from that of **1** or that of the product obtained by heating **1** at 125 °C for 23 h. Further, the ^{1}H NMR spectrum of the new phase was identical to that of an authentic sample of **1**. Preliminary DSC experiments were in agreement with the X-ray powder diffraction studies, and showed an endotherm at ca. 85 °C. Attempts to grow crystals of the new phase at higher temperatures and/or from different solvents were unsuccessful.

CONCLUSIONS

We have found that structural principles developed originally by Etter[8] may be used to produce a (substituted pyridinium) - propynoate material, **1**, with short acetylene-acetylene contacts. This phase does not polymerize when exposed to ^{60}Co γ-rays, consistent with the observation that only metal salts of propynoic acid react when exposed to γ-rays. However, **1** undergoes a phase change upon heating to 90 °C; this new phase reacts upon further heating to give (*E* and *Z*)-4-(1-pyrrolidino)-pyridinium-1-acrylate (**2** and **3**). While the first step in this process is likely to involve abstraction of the proton attached to N by the propynoate anion, the structure-reactivity relationships for reactions of this type must follow from the study of other reactive phases, prepared using different proton acceptors. This work is currently underway in our laboratory.

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