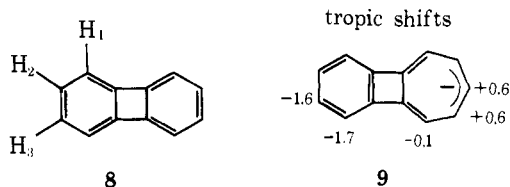


Analysis of the AA'XX' pattern for the benzo protons of **2** yielded $J_{9,10} = 8.00$ and $J_{10,11} = 7.06$ Hz.¹⁸ This indicates a bond fixation in the direction of **6** and contrasts with that in biphenylene (**8**) ($J_{1,2} = 6.89$, $J_{2,3} = 8.23$ Hz)¹⁹ and several of its analogues.²⁰ Anion **2** is the first biphenylene analogue in which the four-membered ring exists in the dimethylenecyclobutene form rather than the tetramethylenecyclobutane form.²¹ When one takes into account the strain of the four-membered ring,²² the bond fixation in the benzo ring of **2** is comparable to that in naphthalene²³ and is clearly characteristic of a benzannelated $4n + 2$ π -electron system. In contrast, the degree of bond fixation (or distortion) in the seven-membered ring of **2** ($J_{2,3} = 7.60$ Hz) is more characteristic of a $4n$ π -electron ring than of a $4n + 2$ π -electron ring (such as in **5**, where $J_{2,3} = 9.0$ Hz¹¹).



The influence of ring currents is most clearly illustrated by the downfield shift of H_9 and H_{10} in **2** compared to **5** despite the large increase in π -electron density in the former compound. The change in chemical shifts caused by net changes in ring currents which occur on adding two electrons to the lowest unoccupied molecular orbital (LUMO) in cation **5** to give anion **2** are termed "tropic shifts".¹⁷ These result from the quenching of any paramagnetic ring currents associated with the LUMO in **5** and from the net diamagnetic or paramagnetic ring currents associated with the LUMO and the highest occupied molecular orbital in **2**. Tropic shifts (see **9**) are given by the difference between the charge-induced chemical shifts for **2** (calculated by correcting the chemical shifts in **5** for the change in π -electron density on going from **5** to **2**) and the observed chemical shifts for **2**. The large diatropic shifts (negative values) at H_9 and H_{10} can be explained by a quenching of a peripheral paramagnetic ring current in **5** coupled with a significant peripheral diamagnetic ring current in **2**. Interestingly, H_3 and H_4 suffer small paratropic shifts which can be attributed to the dominant influence of a paramagnetic ring current in the seven-membered ring of **2**. The significance of these shifts lies in their contrast with the large diatropic shift observed for H_{10} and indicate a local paramagnetic ring current of *over 2 ppm* in the seven-membered ring of **2**.

In summary, anion **2** behaves as *both* a peripheral $4n + 2$ π -electron system and as a local $4n$ π -electron system. This anion is therefore an example of that rare class of compounds which display properties characteristic of both aromatic and antiaromatic π -electron systems.^{2a}

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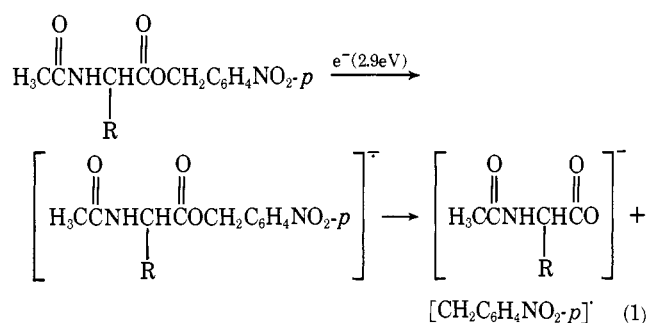
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Gas Phase Carboxylate Anions from *N*-Acetyl-*p*-nitrobenzyl Amino Acid Esters

Sir:

Gas phase carboxylate anions of the *N*-acetyl derivatives of alanine, valine, and proline have been efficiently generated in a mass spectrometer. The process involves the dissociative resonance capture¹ of 2.9-eV electrons by the *p*-nitrobenzyl-*N*-acetyl amino acid derivative as illustrated in eq 1 below. The *p*-nitrobenzyl group is utilized to increase the electron affinity of the molecule and thereby enhance the efficiency of the initial electron capture which gives the anion radical intermediate postulated in eq 1. The subsequent cleavage of the carbon oxygen bond of the ester occurs almost exclusively to give the carboxylate anion and not the *p*-nitrobenzyl anion. This is shown in Table I by the relative intensities of the *m/e* 136 and the *M* - 136 peaks. At this electron voltage² (2.9 eV), the *m/e* 136 peak representing the *p*-nitrobenzyl anion was only 11% as large as the carboxylate anion (represented by the *m/e* 130 peak) in the alanine derivative and was not observed in the proline derivative. Thus, disregarding the *m/e* 46 peak (NO_2^-), the *N*-acetyl carboxylate anion represents over half the total ion current in each of the derivatives.



The sensitivity of the instrumental technique and the simplicity of the experimental procedure are illustrated by the fact that only 1 μg of the derivatives was necessary to obtain the observed data in Table I. The esterification and acetylation were carried out in the same reaction vial using 5-10 μg of the free amino acids and no further purification was necessary.³

The specific electron energy (2.9 eV) used to generate the *N*-acetyl carboxylate anions was determined by obtaining

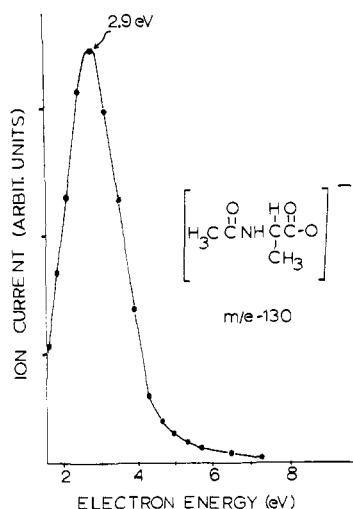


Figure 1. The ionization efficiency curve for the m/e 130 anion from *p*-nitrobenzyl-*N*-acetylalanine.

Table I. Gas Phase Anions of Amino Acid Derivatives^a (2.9 eV electrons)

Peak	Alanine- m/e	Valine- m/e	Proline- m/e
M - 136 ^b	130 (100%)	158 (87%)	157 (32%)
M - 136 - 42 ^b	88 (66%)	116 (7%)	—
46 ^b	(25%)	(100%)	(100%)
136	(11%)	(7%)	—

^a The *N*-acetyl-*p*-nitrobenzyl esters of these compounds were used.

^b m/e 136 represents the *p*-nitrobenzyl group, m/e 42 represents CH_2CO , and m/e 46 represents NO_2^- ; all peaks greater than 5% of the respective base peaks are shown.

ionization efficiency (IE) curves. The IE curve for the carboxylate anion of *N*-acetylalanine (m/e 130) is shown in Figure 1. This curve exhibited a dissociative resonance capture maximum at 2.9 eV which was the same as obtained for the analogous anions from the valine and proline derivatives. The IE curve also showed that the energy requirement for the efficient generation of the carboxylate anion is quite specific and a variation of less than 1 eV from the 2.9 eV maximum would cause a substantial decrease in the ion current.

It is important to note that these gas phase anions are being generated with electron energies substantially below the appearance potentials for any positive ionization of these molecules. This helps to explain the lack of extensive fragmentation and also illustrates that significant interactions are indeed occurring between low energy electrons and molecules in the positive ion mode of a mass spectrometer, even though they cannot be observed.

A wide variety of the more polar classes of bioorganic compounds such as amino acids and related compounds undergo extensive decomposition under conventional 70 eV electron impact.⁴ In the past few years, a number of alternate ionization techniques have been developed in an attempt to circumvent this problem. The techniques more widely used include field ionization,⁵ chemical ionization,⁶ and more recently field desorption.⁷ With these techniques, extensive fragmentation of sensitive bioorganic compounds is minimized and molecular ions are more easily observed.

The generation of gas phase anionic species, especially in molecules such as amino acid derivatives where extremely stable anions can be formed, has been shown to be a very low energy process. Extensive fragmentation is not observed and the anions that are produced, at least in the above examples,

can be easily correlated with the structure of the molecules. Furthermore, from a practical analytical viewpoint, ions from possible volatile contaminants such as oil, grease, plasticizers, etc. are not formed with the 2.9-eV electron energy and, thus, would not produce interfering background.

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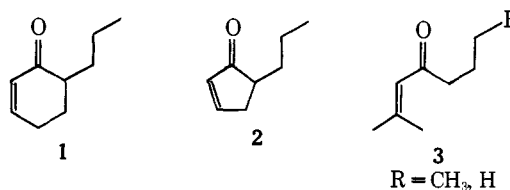
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Photochemical γ -Hydrogen Abstraction in an α -Acetylenic Ketone. Comparison with an Analogous Enone

Sir:

Irradiation of alkanones and alkyl aryl ketones frequently leads to γ -hydrogen abstraction followed by β -cleavage and cyclobutanol formation.¹ In the case of α,β -unsaturated ketones, the efficiency of γ -hydrogen abstraction is very much lower in the six-membered enone **1** than in the five-membered analogue **2**² while the acyclic compounds **3** are photochemically inert.³ Since other enone photoreactions depend on double bond rigidity⁴ and since acyclic enones are known to undergo geometric isomerization,^{4,5} it is reasonable that the lower efficiency of the flexible compounds is due to rapid radiationless decay induced by olefin twisting.⁶ However, it should be added that olefin isomerization does not always preclude other reactions of excited enones.^{5,7,8}



We reasoned that an α -acetylenic function might have virtually no deactivating effect on the photoreactivity of the carbonyl group since rotation about the cylindrically symmetric triple bond can hardly lead to crossing of the excited state potential surface with that of the ground state. Of course, other radiationless decay pathways might operate in ynones⁹ but since only one photochemical study of such compounds has