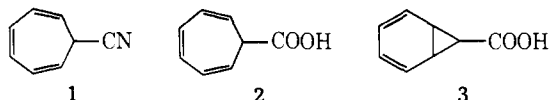


Direct Observation of "Buchner's Acid" Using ^{13}C and ^1H Nuclear Magnetic Resonance Spectroscopy

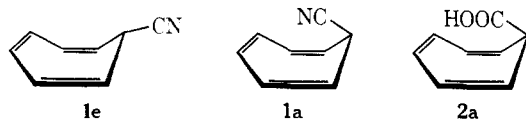
Sir:

In 1970 Bushweller, Sharpe, and Weininger¹ reported the first direct observation of ring inversion for a 7-mono-substituted cycloheptatriene in the case of 7-cyanocyclohepta-1,3,5-triene (**1**). Similar results were mentioned for cyclohepta-1,3,5-triene-7-carboxylic acid (**2**). **2** is one of the four Buchner acids,² long formulated as norcaradiene derivative **3** and later shown by Doering et al.³ on the basis of proton NMR spectroscopy to possess the cycloheptatriene structure **2**.



We now wish to report that Buchner's acid **3** does indeed exist. In the course of low-temperature ^{13}C NMR measurements in connection with work on fluxional systems of the norcaradiene-cycloheptatriene type,⁴ we noticed remarkable differences in the spectral behavior of compounds **1** and **2**⁵ (Figure 1). The spectrum of **1** shows all the features expected for a molecule undergoing ring inversion. After initial line broadening, a splitting of all resonances—except that of C-3,4—is observed until finally a superposition of the ^{13}C NMR spectra of **1e** and **1a** is found (Table I). From the signal intensities $K(-132.5^\circ) (p(\mathbf{1e})/p(\mathbf{1a})) = 3.9$ and $\Delta G^\circ (-132.5^\circ) = 380$ cal/mol is calculated, in fair agreement with the ^1H NMR results ($K(-155^\circ) = 28$, $\Delta G^\circ(-155^\circ) = 780$ cal/mol).¹

In contrast, **2** shows significant line broadening only for the resonances of C-1,6 and C-7. After "coalescence" has apparently occurred since the lines sharpen again, no signals belonging to a second conformer could be detected. This finding can be typical for dynamic processes where the concentration of the two isomers differs strongly and where in the slow exchange limit only one of them is observable due to signal overlap and low signal intensity.^{4,6,7} In the case of **2** this could be explained with the increased steric repulsion present in the axial conformer **2a** due to the bulkiness of the carboxyl group as compared to the linear cyano group. On the other hand, the selective broadening of the C-1,6 and C-7 resonances raised doubt on the existence of a ring inversion process and suggested instead the valence tautomerism $\mathbf{2} \rightleftharpoons \mathbf{3}$ as the origin of the line shape changes.



Accordingly, the ^1H NMR spectrum of **2** was reinvestigated, and our findings clearly support the existence of a fluxional system $\mathbf{2} \rightleftharpoons \mathbf{3}$ (Figure 2). After line broadening is observed for the triplet of H(7), this resonance sharpens

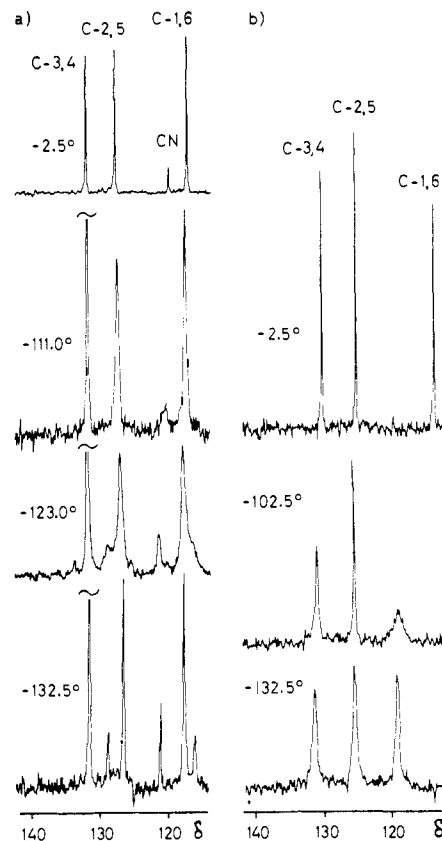


Figure 1. Temperature dependence of the 22.6-MHz ^{13}C NMR spectra of **1** (concentration 0.54 M) and **2** (concentration 0.46 M) in the region of olefinic carbon resonances: solvent $\text{C}_2\text{H}_5\text{Cl}-\text{CD}_2\text{Cl}_2$ (4:1); δ values refer to internal TMS, assignments see Table I.

again below -110° and a new signal of low intensity appears at δ 0.52, within the anticipated absorption range for H(7) in structure **3**. No other new signal in the aliphatic region was found and the δ 3.83 absorption reported by Bushweller et al.¹ could not be confirmed. As a consequence, the H(1,6) resonance of **3** was believed to coincide with the H(7) resonance of **2** at δ 2.63. That this is indeed the case is demonstrated in Figure 3 that shows the low temperature ^1H NMR spectra of 7-deuterio-**2**.⁸ In the slow exchange limit a new signal appears at δ 2.65, the typical region for H(1,6) resonances of norcaradienes.⁹ Finally, the low field shift observed for δ (H-7) in the fast exchange limit (Figure 2) is indicative of a dynamic process between **2**, existing predominantly as conformer **2e**,¹⁰ and a high energy isomer in which H(7) is strongly shielded. Only the norcaradiene fulfills this requirement, since in **2a** H(7) is deshielded^{11,12} with respect to **2e**.

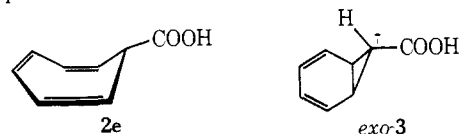


Table I. $\delta(^{13}\text{C})$ Values of **1** and **2** at Various Temperatures; Reference Internal TMS

	1e \rightleftharpoons 1a			1e	1a	2 \rightleftharpoons 3		2
	-2.5°	-111.0°	-123.0°			-2.5°	-102.5°	
C-1,6	117.2	117.5	117.8	118.0	116.5	114.8	119.8	119.7
C-2,5	127.6	127.4	127.0	126.9	129.2	126.3	126.1	126.1
C-3,4	131.8	131.8	131.8	131.9	131.9	131.3	131.6	131.8
C-7	30.4	30.4	31.0	31.2	28.2	43.8	44.5	45.0
$\text{C}\equiv\text{N}$	119.9	120.2	121.4	121.5	117.7			
$\text{C}=\text{O}$						180.6	181.0	180.9

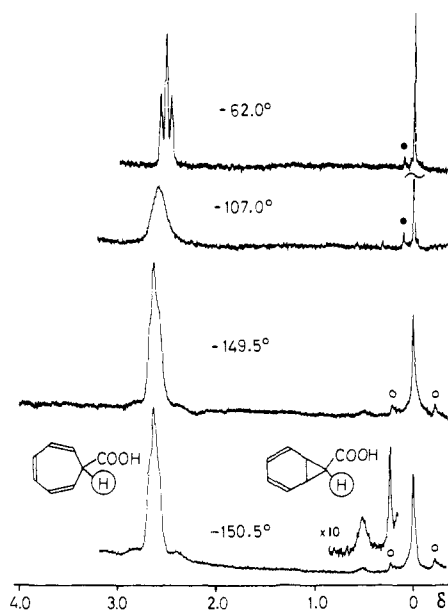


Figure 2. Temperature dependence of the 100-MHz ^1H NMR spectrum of **2** in the region of aliphatic ^1H resonances: internal reference TMS, solvent vinyl chloride, concentration 0.42 M; (●) unidentified impurity, (○) spinning side bands.

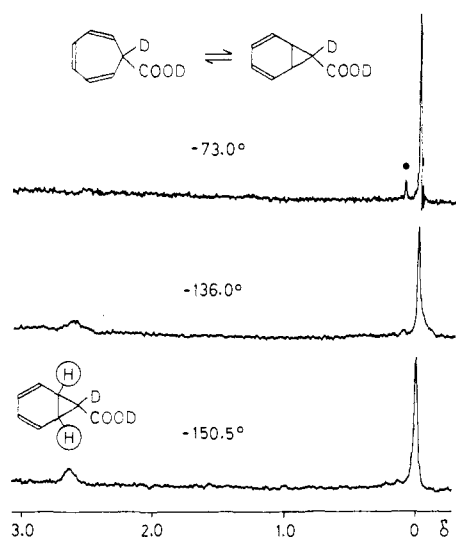


Figure 3. Temperature dependence of the 100-MHz ^1H NMR spectrum of 7-deuterio-**2**; experimental conditions as above; (●) unidentified impurity.

From peak area measurements the concentration of **3** was determined as ca. 3%, leading to $\Delta G^\circ(-150^\circ) = 900$ cal/mol in favor of **2**. According to the high field absorption of H(7) we conclude that **3** exists as the *exo* isomer *exo*-**3**. Using model compounds¹³ δ 0.97 or 0.87 ppm is predicted, in good agreement with our findings. Additional support comes from the half-width of ca. 10 Hz measured for the signal of H(7) in **3** at -150° that is only consistent with a *trans* coupling constant.¹⁹

Our results and findings recently reported by Klärner²⁰ for 7-methyl-**1** and 7-methyl-**2** show that an *exo*-carboxyl group in 7-position is more effective in stabilizing the norcaradiene than an *exo*- or *endo*-cyano group. This conforms to the MO model of norcaradiene stabilization,^{21,22} since according to MO energies²³ the COOH group should interact more strongly with the Walsh orbital than the cyano group. For *endo* substitution the situation is complicated by steric^{4,20} and additional electronic²⁴ effects.

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- (12) The unsymmetry shown by the broadened H(7) resonance of **2** (Figure 2, -107°) also indicates that coalescence occurs with a high field signal. However, in order to use this effect unambiguously, deuterated solvents are necessary since the line shape depends critically on phase adjustments for the large solvent peak.
- (13) Cyclopropane δ 0.22;¹⁴ cyclopropyl carboxylic acid δ (CH) 1.59;¹⁵ 2,3-benzonorcaradiene δ (H_{endo}) -0.35 ;¹⁶ 2,3-benzonorcaradiene-*exo*-7-carboxylic acid δ (H_{endo}) 0.92;¹⁷ tricyclo[4.3.1.0^{1,6}]decadiene-2,4 δ (H_{endo}) -0.40 , (H_{exo}) 1.42.¹⁸
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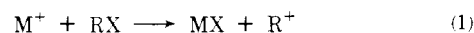
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Reactions of Alkali Ions with Organic Molecules in the Gas Phase. Low Energy Pathways for Carbonium Ion Formation and Novel Methods for Generating Alkali Ion Complexes with π - and n -Donor Bases

Sir:

While the reactivity of alkali atoms with halogenated hydrocarbons has been recognized for several decades, the interesting possibility that alkali ions may also undergo rapid reactions with these species has not been explored. We have recently demonstrated that halide ion transfer reactions between carbonium ions are rapid and can be employed to determine R^+-X^- heterolytic bond energies, $D(R^+-X^-)$.¹⁻³ A comparison of M^+-X^- heterolytic bond energies of alkali halides to $D(R^+-X^-)$ for various carbonium ions R^+ , Table I, reveals several examples of reaction 1 which are exothermic.



To investigate such reactions a thermionic source⁴ was mounted inside the source region of an ICR cell.^{5,6} While the spectrometer was operated in the drift mode for the studies reported herein, we have also performed trapped ion experiments using the thermionic source.

Typical results are shown in Figure 1. Double resonance