be possible to use these electrosynthetic methods to generate fullerides for ion-pairing studies by ESR spectroscopy. Such work is currently underway.

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X-ray Crystal Structure of the First Quaternary 1-Bicyclo[1.1.1]pentane Salt. The Shortest "Nonbonding" Carbon–Carbon Interaction Documented

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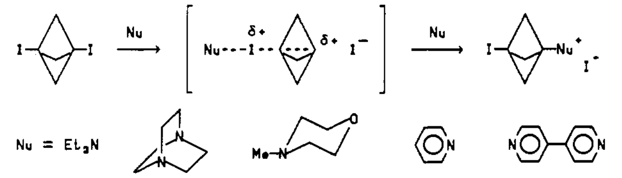
The simplest strained-cage molecule, bicyclo[1.1.1]pentane and its derivatives, e.g., [1.1.1]propellane, have received significant attention the last few years.[1] The shortest (1.83–1.91 Å) C_1–C_3 nonbonding distance ever reported, found in the bicyclo[1.1.1]pentanes,[2] leads to unusual chemical reactivity as well as unusual spectral properties for these compounds.

Recently it was proposed that the bicyclo[1.1.1]pentane framework may be used for the preparation of nanotechnology-important substrates[3] due to its unique through-cage electron-transfer ability.[4] For this purpose, however, the C_1–C_3 interatomic distance is critical, so that the task of finding 1,3-disubstituted bicyclo[1.1.1]pentanes with the shortest C_1–C_3 contacts is important.

With this goal in mind, we investigated pyridine salts containing the 3-iodobicyclo[1.1.1]pentane moiety which have recently been prepared by way of an unusually fast quaternization of tertiary amines and azoles with 1,3-diiodobicyclo[1.1.1]pentane:[5]



Considering the fact that in these salts the bicyclo[1.1.1]pentane moiety is substituted by a strong electron-withdrawing group (e.g., 1-pyridyl) with a full positive charge, these molecules could have very short C_1–C_3 distances. According to Wiberg,[6] the addition of strong electron-withdrawing groups attached to C_1 or C_3 would decrease the interatomic distance, whereas electron-donating substituents would increase this distance. Known X-ray data[2] are in good agreement with these predictions (see Scheme I).

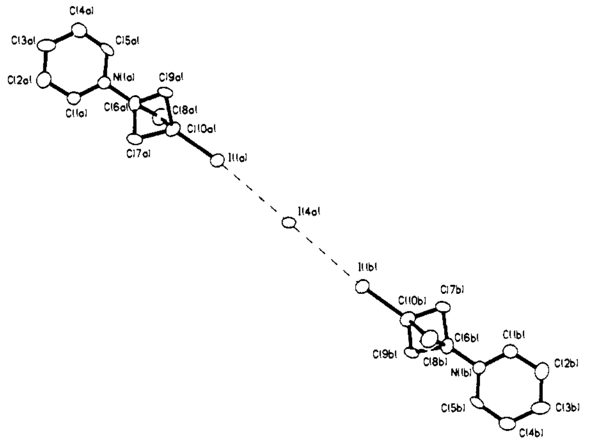
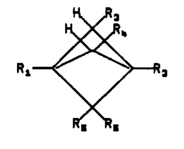


Figure 1. Molecular structure and labeling scheme for **1** (50% thermal ellipsoids): C(10)–C(6), 1.80 (2) Å; I(1)–I(4), 3.745 (1) Å; ∠I(1a)–I-(4a)–I(1b), 180°; N(1)–C(6), 1.47 (2) Å; C(10)–C(7), 1.55 (2) Å; C-(10)–C(8), 1.56 (2) Å; C(10)–C(9), 1.56 (1) Å; ∠C(10)–I(1)–I(4), 172.1°.

Scheme I



R_1	R_2	R_3	R_4	R_5	R_6	C_1 - C_3	Ref.
CCl_3	Cl	H	H	H	H	1.83(2) Å	2a
CCl_3	I	H	H	H	H	1.835(7)Å	2a
CH_3	COOH	H	H	H	H	1.873(2)Å	2b
COMe	COMe	H	H	H	H	1.874(6)Å	2c
H	H	H	H	Ph	OCONHPh(Br)	1.89 Å	2d
H	H	COOMe	COOMe	$-OCH_2CH_2O-$		1.903(3)Å*	2e
CH_3	COOMe	H	H	Cl	Cl	1.903(3)Å	2f

*For one of the stereoisomers -[1.898(3); 1.902(3); 1.903(3); 1.903(6); 1.907(3) Å] for other.

The crystallographic data[7] obtained by us for one compound of this type, 1-(1-pyridinio)-3-iodobicyclo[1.1.1]pentyl iodide/triiodide (**1**), did confirm our expectations, but it also gave important information about the structure of this new class of strained-cage salts (Figure 1).

The C_1–C_3 [C6–C10 on Figure 1] distance in **1** is extremely short (1.80 (2) Å). To our knowledge, this is not only the shortest nonbonding contact for bicyclo[1.1.1]pentanes but also for any known organic compound.

Another intriguing feature of this salt is the nonequivalence of two existing iodo anions in the crystal structure of **1**. The I_3^- anion has the usual structural parameters.[8] The I^- anion, on the other hand, occupies a very specific site in the crystal: it is located exactly between two cationic units (Figure 1), so that the angle I(1a)–I(4a)–I(1b) is 180° within experimental error. In addition, the interatomic distance between these iodine atoms is shorter than the sum of their van der Waals radii (3.745 vs 4.30 Å[9]), indicating

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[7] Crystals of **1** were obtained by slow evaporation of a diluted methanolic solution of 1-(1-pyridyl)-3-iodobicyclo[1.1.1]pentane iodide, which contained additional I_2: $(C_{10}H_{11}I_3N)_2$, triclinic, $P\bar{1}$; $a = 6.173$ (1) Å, $b = 9.607$ (2) Å, $c = 13.067$ (2) Å; $\alpha = 74.50$ (1)°, $\beta = 76.86$ (2)°, $\gamma = 72.03$ (2)°; $V = 701.3$ (2) Å^3, $Z = 1$, $d_{calcd} = 2.490$ g/cm^3, μ(Mo Kα) = 6.586 mm^{-1}. $R = 5.44\%$ ($R_w = 7.56\%$) for 1680 reflections at 173 K, $3.5 \leq 2\theta \leq 52°$, $F_o \geq 4.0\sigma(F_o)$, on a Siemens R3m/v diffractometer with Mo Kα ($\lambda = 0.71073$ Å) and a graphite monochromator.

[8] For X-ray data on I_3^- and related poly(iodine) anions, see: (a) Havinga, E. E.; Wiebenga, E. H. *Acta Crystallogr.* **1958**, *11*, 733 and references therein. (b) Hach, R. G.; Rundle, R. E. *J. Am. Chem. Soc.* **1951**, *73*, 4321. (c) Havinga, E. E.; Boswijk, K. H.; Wiebenga, E. H. *Acta Crystallogr.* **1954**, *7*, 487. (d) Hendrixson, T. L.; Horst, M. A.; Jacobson, R. A. *Acta Crystallogr.* **1991**, *C47*, 2141.

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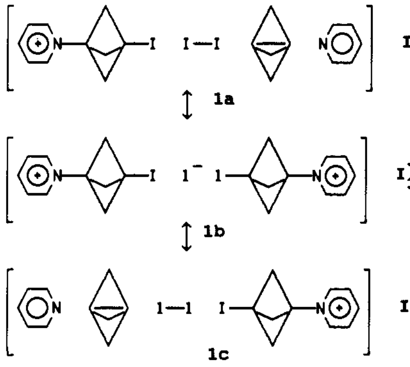
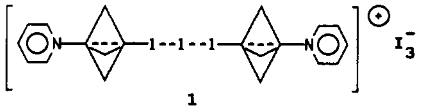
some kind of interaction. Other structural characteristics of this molecule, such as interatomic distances and angles in the pyridine ring[10] and the bicyclo[1.1.1]pentane moiety,[2] are normal.

From all these data it is clear that the real structure of the compound is more complex and may be represented as the resonance hybrid of structures (**1a** ↔ **1b** ↔ **1c**):



which can be depicted as



1

The extremely short nonbonding intercage distance in **1** is then due to contributions from resonance structures **1a** and **1c**, each of which contains one full ([1.1.1]propellane-type) C_1–C_3 bond, as well as the short I–I–I distance between the two cage units.

We believe that such substituted azinium salts may well deserve serious attention as possible components for the creation of materials with unusual electronic properties.

Supplementary Material Available: Tables of additional X-ray data including coordinates, bond distances, bond angles, and thermal parameters for **1** (8 pages). Ordering information is given on any current masthead page.

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Kinetic Isotope Effects on the Hydroxide Ion Catalyzed Enolization of Acetone: Relationship between Deuterium and Tritium Isotope Effects

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The hydroxide ion catalyzed enolization of acetone is a prototype ketone ionization reaction, and it is disturbing therefore that deuterium and tritium isotope effects reported for this process[1] give a Swain–Schaad exponent relating the two effects, eq 1, that is anomalously low: $x = 1.08$. This value is much less than x

$$(k_H/k_D)^x = k_H/k_T \qquad (1)$$

= 1.44 originally predicted by Swain and Schaad on the basis of a zero-point energy formulation of isotope effects,[2] and it is well outside the limits, $x = 1.33$–1.58, required by more complete theory.[3] Calculations on model systems[4] also indicate that exponents as low as $x = 1.08$ are quite improbable. This discrepancy in a simple chemical system is especially serious because deviations from the Swain–Schaad relationship have been used lately to diagnose tunneling in enzyme-catalyzed reactions.[5] We have reexamined the acetone system using a new approach to determining the tritium rate constant, k_T, and also paying particular attention to the efficiency of the bromine scavenging method used to determine the protium rate constant, k_H. With this reexamination, we now obtain isotope effects that give a Swain–Schaad exponent in complete agreement with theory.

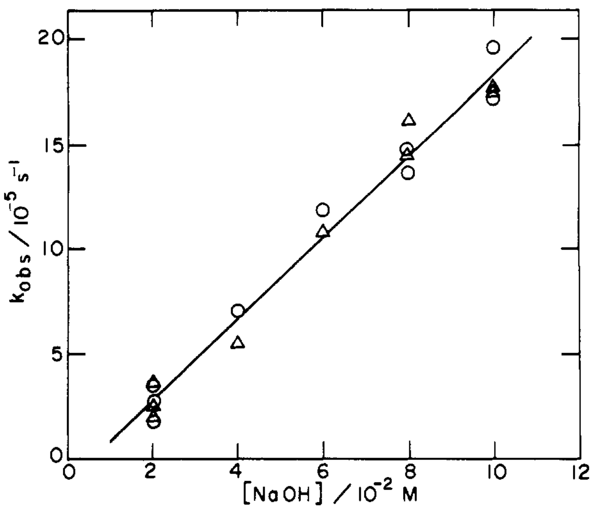

Figure 1. Relationship between sodium hydroxide concentration and observed rate constants for tritium exchange between acetone and water in aqueous solution at 25 °C, ionic strength = 0.10 M (NaCl), measured by monitoring the acetone (○) and water (△) tritium NMR signals.

The original tritium isotope effect was based upon rates of detritiation of labeled acetone in aqueous solution determined by a technique that involved a difficult separation of acetone from water.[1] We have chosen to use tritium NMR spectroscopy to monitor the exchange of tritium between acetone and water directly in situ,[6] thus avoiding the troublesome acetone–water separation.

Acetone-t_1 (1.2 Ci mmol^{-1}) was prepared by base-catalyzed exchange between acetone and tritiated water; the product gave a single tritium NMR signal at $\delta = 2.1$ ppm. When this substance was dissolved in dilute aqueous sodium hydroxide solution, this signal decayed and another resonance at $\delta = 4.7$ ppm, attributable to H_2O-t_1, appeared. Changes in intensity of both signals obeyed the first-order rate law well, and least-squares fitting to exponential functions gave observed rate constants for the rise and the decay which, as Figure 1 shows, agree well with each other. These rate constants increase linearly with sodium hydroxide concentration (Figure 1), and least-squares analysis gives the hydroxide ion catalytic coefficient, $k^T_{HO^-} = (1.95 \pm 0.07) \times 10^{-3}$ M^{-1} s^{-1}. This is 20% lower than the value reported before.[1]

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