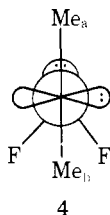


Figure 1. Experimental (left) and computer-simulated  $^1\text{H}$  NMR spectra of  $[\text{Me}_2\text{NSF}_2]^+$  (1). The experimental spectra were obtained in  $\text{SO}_2$  solution.



trum collapses and emerges as a triplet, while the  $^{13}\text{C}$  and  $^{19}\text{F}$  spectra become a singlet (39.3 ppm) and a septet ( $-16.0$  ppm,  $J_{\text{HCNSF}} = 7.5$  Hz), respectively. These spectral changes are attributed to rotation around the N-S bond becoming rapid on the NMR time scale. Computer line-shape analyses of the  $^1\text{H}$  dynamic NMR spectra indicate that the barrier to N-S rotation in **1** is 14.7 kcal/mol. This result implies that the N-S torsional barriers in aminosulfonium cations are significantly larger than the N-P barriers of the corresponding aminophosphines.<sup>9</sup> Thus, aminosulfonium salts might find use as models for aminophosphine stereochemistry in cases where, because of low N-P torsional barriers, considerable doubt persists regarding the ground-state geometry.

The coordination chemistry of aminosulfonium cations is under active investigation and will be reported in subsequent publications.

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- (4) In some experiments the  $^1\text{H}$  resonance of **1** appeared as a singlet, presumably due to intermolecular exchange by  $\text{F}^-$ . The dynamic NMR spectroscopic experiments described below were conducted under carefully controlled conditions on very pure **1**.
- (5)  $^{19}\text{F}$  chemical shifts in parts per million relative to external  $\text{CCl}_3\text{F}$ ;  $^{13}\text{C}$  chemical shifts in parts per million relative to external  $\text{Me}_4\text{Si}$ .
- (6) The  $^{19}\text{F}$  chemical shift and  $^{11}\text{B}$ - $^{19}\text{F}$  constant of  $\text{BF}_4^-$  have been shown to be markedly dependent on concentration and on the nature of the cation and solvent. See R. Haque and L. W. Reeves, *J. Phys. Chem.*, **70**, 2753 (1966), and references therein. Presumably, the same is true for the "mixed" anions,  $[(\text{Me}_2\text{N})_x\text{BF}_{4-x}]^-$ .
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## Solvolytic of Cyclooctatetraenyl Trifluoromethanesulfonate<sup>1</sup>

Sir:

Cyclic vinyl trifluoromethanesulfonates (triflates) and nonafluoro-*n*-butanesulfonates (nonaflates) solvolyze in suitable solvents<sup>2</sup> with formation of cyclic vinyl cations. The rate of solvolysis of the reaction, and with that the tendency of the cyclic vinyl cations to exist as intermediates, depends on the size of the ring. With the exception of 1-cyclobutenyl nonaflate, which stands out in the cyclic series because of its high solvolysis rate,<sup>3</sup> a steady rise in the rate of solvolysis going from the slowly reacting 1-cyclohexenyl triflate up to the 1-cyclononyl triflate was observed owing to the increasingly easy formation of a stable linear vinyl cation.<sup>2</sup>

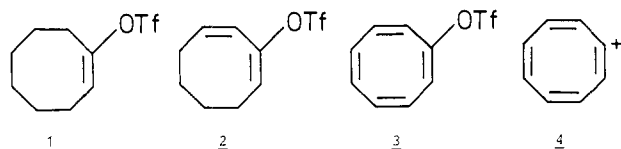
Additional stabilization of cyclic vinyl cations can be achieved by conjugated double bonds in the ring system, when the size of the ring allows orthogonality of the double bonds for a good overlap of the vacant p orbital of the vinyl cation

**Table I.** Solvolysis Products of COT Triflate **3** at Room Temperature

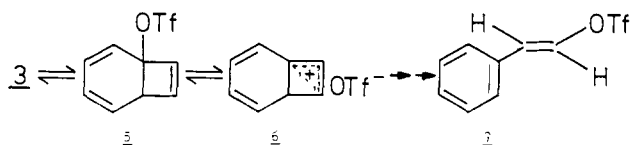
solvents <sup>a</sup>	reaction products, %				COT bromide <sup>b</sup>
	<b>8</b>	<b>9</b>	<b>10</b>	<b>7<sup>b</sup></b>	
absolute TFE	79		5	14	2
absolute EtOH		77	10	11	2
80% TFE	35		43	19	3
50% EtOH		42	42	14	2

<sup>a</sup> In all cases 1.1 mol equiv of pyridine was used as buffer. <sup>b</sup> Percentage of **7** and COT bromide already present in the starting COT triflate **3**.

with the  $\pi$  orbitals of the neighboring double bond. Thus we could recently show<sup>4</sup> that 1,3-cyclooctadien-2-yl triflate (**2**) solvolyzes  $\sim 10^3$  times faster with formation of the corresponding vinyl cation than 1-cyclooctenyl triflate (**1**). Stabi-



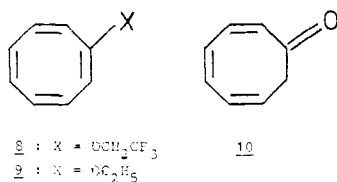
lization for the 1,3-cyclooctadien-2-yl cation relative to 1-cyclooctenyl cation is therefore clearly indicated.<sup>5</sup> Therefore it was of interest to find out whether the cyclic vinyl cation **4** could be generated as an intermediate by solvolysis of cyclooctatetraenyl triflate (**3**) and to investigate the stability of the resultant cation **4** due to the special geometry of this system. Besides the possible formation of ion **4** another feasible reaction path for triflate **3** is the formation of **7** via **5** and **6** analogous to the reported thermal rearrangement of cyclooctatetraenyl bromide (COT bromide).<sup>6</sup>



In this communication we report our results on the solvolysis of cyclic triflate **3**. COT triflate (**3**) was prepared by treating COT bromide<sup>6</sup> with silver triflate in the presence of anhydrous  $\text{Na}_2\text{CO}_3$  in absolute  $\text{CCl}_4$  at room temperature for 2 days.

The COT triflate was purified by condensation at room temperature under vacuum to a precooled trap. COT triflate (**3**):  $^1\text{H}$  NMR broad signal at  $\delta$  5.94 ppm in  $\text{CDCl}_3$ ; IR (film)  $\bar{\nu}$  3040, 1650, 1430, 1225, 1150, 1020  $\text{cm}^{-1}$ . COT triflate (**3**) can be stored for longer periods only at low temperature and contains 2–3% COT bromide and between 11 and 19% *trans*- $\beta$ -styryl triflate (**7**).<sup>7</sup> The valence isomer of COT bromide, the *trans*- $\beta$ -bromostyrene, does not react with silver triflate under these conditions. The valence isomer **7** is formed from COT triflate (**3**) analogously to COT bromide by thermal rearrangement even at room temperature during the long time (2 days) needed for its preparation.

The COT triflate (**3**) thus prepared was solvolyzed at room temperature in absolute 2,2,2-trifluoroethanol (TFE), absolute ethanol, 80% TFE, and 50% ethanol, solvent systems of different nucleophilicity and ionization strength. The products

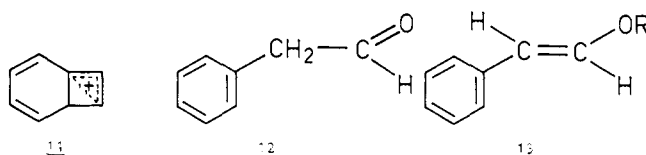
**Table II.** Solvolysis<sup>a</sup> Rates of COT Triflate **3** at 1 °C

solvent	$k, \text{s}^{-1}$	$t_{1/2}, \text{s}$
97% TFE	$0.72 \pm 0.02 \times 10^{-2}$	96
50% EtOH	$0.3 \pm 0.1 \times 10^{-2}$	210

<sup>a</sup> Determined by a continuous titration method.<sup>10</sup>

obtained were the corresponding enol ethers **8** and **9<sup>8</sup>** and cyclooctatrienone (**10**).<sup>9</sup> They were separated by preparative gas chromatography and identified by capillary gas chromatography and by spectroscopic comparison with authentic samples. The results are summarized in Table I. *trans*- $\beta$ -Styryl triflate (**7**) and COT bromide do not play any role in the solvolysis reactions as they remain unchanged under these reaction conditions.

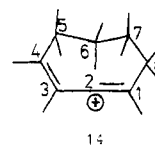
The exclusive formation of only eight-membered-ring products is evidence for the generation of the intermediate cyclic vinyl cation **4** that gets captured by solvent. If a homocyclopropenium cation (**11**) were involved as an intermediate,



then aldehyde **12** and enol ether **13** should also have been formed during the solvolysis reaction. We could not detect any of these products. The solvolysis rates of COT triflate (**3**) given in Table II are further proof for the formation of the intermediate cyclic vinyl cation **4**. Extrapolation of the reported solvolysis rates in aqueous ethanol to the temperature of 1 °C gives a value of  $3.4 \times 10^{-9} \text{ s}^{-1}$  and  $3.6 \times 10^{-5} \text{ s}^{-1}$  for the triflates **1** and **2**.<sup>4</sup> Therefore the rate of solvolysis of COT triflate (**3**) (Table II) is  $\sim 10^6$  times faster than that of **1** and  $10^2$  times faster than that of **2**.

The  $10^2$  times faster solvolysis rate of COT triflate (**3**) compared with that of the cyclooctadienyl triflate (**2**) can be explained as follows. The conjugation effect of the double bonds in **2** is still present in the corresponding vinyl cation **14**. This conjugation obstructs the favorable overlap of the vacant p orbital of the cation **14** with the neighboring double bond and must be overcome before its stabilization is possible. Yates and Perié<sup>11</sup> have shown that such steric effects are possible; for example ortho-disubstituted  $\alpha$ -styryl bromides react  $\sim 10^5$  times faster than the corresponding unsubstituted bromide. A pronounced effect of this order is not to be expected in the case of **2** since the flexibility of the ring is limited.

Dreiding models of **14** show that one of the hydrogen atoms at C-6 in **14** lies very close to C-2. The strain of **14** is increased by twisting the ring, whereby the eclipsed conformations between the hydrogen atoms of C-5, C-6, and C-7 are selectively unfavorable. Their steric interactions will be even increased by twisting the transannular C-6 atom out of the ring. In all possible conformational maneuvers the overlap of the empty p orbital with the neighboring double bond was not found to be optimal. In the most acceptable case an angle of  $\sim 30^\circ$  was found between the  $\pi$  orbitals of the neighboring double bond and the vacant p orbital, which shows only a modest stabilization of **14**.



On the other hand the hard tub form of **3** allows instant stabilization of the vinyl cation without any conformational

change. Transannular interactions do not occur and the positions of the hydrogen atoms in **4** do not differ significantly from their positions in **3**.

From the activation enthalpies for the valence tautomerization of cyclooctatetraene (28.1 kcal/mol),<sup>12</sup> phenylcyclooctatetraene (25.1 kcal/mol),<sup>12</sup> and COT bromide (23.1 kcal/mol),<sup>6</sup> the half-life of COT bromide was calculated to be 31 days at room temperature.<sup>13</sup> It is then reasonable to assume that the value for the valence tautomerization of COT triflate (**3**) also lies in the same range. Therefore the slow reaction path **3** → **5** → **6** plays no role in the fast solvolysis reaction of COT triflate since only eight-ring products were obtained from the solvolysis.<sup>14</sup>

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## Unusual Coordination of the $\alpha$ -Dioxime Ligand in Bis(camphorquinone dioximato)nickel(II)

Sir:

Metal complexes<sup>1</sup> of the dimethylglyoximate ligand (HDMG<sup>-</sup>) have served as models for vitamin B<sub>12</sub>,<sup>2</sup> have been shown to have some one-dimensional metallic properties,<sup>3</sup> and have long been of importance in analytical chemistry.<sup>4</sup> In all of the known structures, the HDMG<sup>-</sup> ligand behaves as a bidentate ligand coordinating to the metal through both nitrogen atoms.

Our interest in these compounds evolved from previous studies of optically active ligands<sup>5</sup> and a desire to prepare complexes with optically active  $\alpha$ -dioxime ligands. We expected these complexes to have catalytic properties similar to those known for Co(HDMG)<sub>2</sub>.<sup>6</sup> The chosen ligand,  $\gamma$ -camphorquinone dioxime (H<sub>2</sub>CQD), was prepared from *d*-camphor according to the procedures of Forster.<sup>7</sup> <sup>1</sup>H NMR studies<sup>8</sup> and an X-ray structural study<sup>9</sup> indicate that this  $\gamma$  isomer

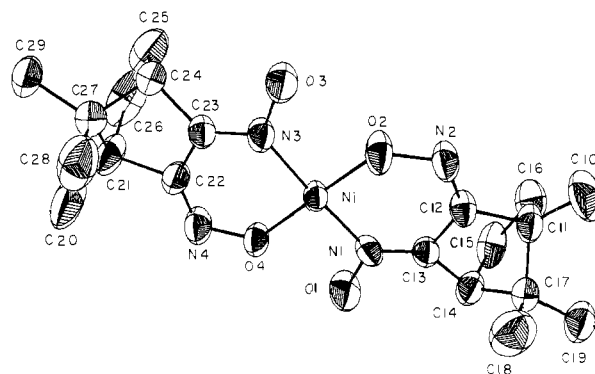
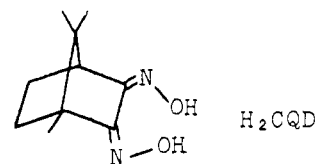


Figure 1. Computer-generated perspective drawing of Ni(HCQD)<sub>2</sub>.

has a syn structure with the OH group orientations as shown at the N atoms. Recently, complexes of the  $\alpha$ ,  $\beta$ , and  $\delta$  isomers of camphorquinone dioxime were reported to catalyze the



cyclopropanation of olefins, and it was suggested that these complexes had structures involving N-O as well as N-N ligand bonding.<sup>10</sup>

The nickel(II) complex was prepared by mildly refluxing a MeOH solution of 0.64 mmol of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 1.28 mmol of H<sub>2</sub>CQD for 10 min. After adding 1.28 mmol of NaOMe in MeOH, the solution was refluxed for an additional 2 h. Following filtration while warm, the solution was evaporated under vacuum to a green solid, which was dissolved in a minimum volume (~10 mL) of CH<sub>3</sub>CN. The solution was filtered immediately and allowed to stand overnight whereupon reddish brown tetrahedral crystals of Ni(HCQD)<sub>2</sub> formed in 20% yield. Anal. (C<sub>20</sub>H<sub>30</sub>N<sub>4</sub>O<sub>4</sub>Ni) C, H, N.

A single tetrahedral crystal of Ni(HCQD)<sub>2</sub> ~0.4 mm on an edge was chosen for the X-ray diffraction study. The observed Laue symmetry and extinctions correspond to the orthorhombic space group *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> with *a* = 13.175 (1), *b* = 13.652 (2), *c* = 12.031 (3) Å; *Z* = 4; and  $\rho_{\text{calcd}} = 1.378$  g/mL. Four octants of data were collected on a four-circle diffractometer designed and built in the Ames Laboratory<sup>11</sup> using graphite monochromated Mo K $\alpha$  X-rays ( $\lambda = 0.70954$  Å) up to a  $2\theta$  limit of 60°. Of the 11 562 measured intensities 7923 were judged observed ( $I > 3.0\sigma I$ ). Correction for Lorentz and polarization effects and averaging of equivalent data yielded 2253 independent reflections. No correction was applied for absorption and an extinction correction was made with  $g = 4.5 \times 10^{-7}$ . The heavy atom was readily located on a Patterson map.<sup>12</sup> Full-matrix least-squares refinement<sup>13</sup> of the structure with anisotropic thermal parameters and fixed hydrogen positions yielded a conventional residual *R* = 0.066 and a weighted residual *R* = 0.085. A computer-generated perspective view of the essential configuration of the ligand and the coordination sphere around the nickel atom is shown in Figure 1.

The six-membered rings give the Ni atom an almost square-planar configuration. The distances from Ni to O-2, O-4, N-1, and N-3 are 1.820 (4), 1.840 (3), 1.859 (4), and 1.851 (4) Å, respectively. The HCQD<sup>-</sup> ligand coordinates to the Ni via N and O donor atoms rather than the common N-N coordination characteristic of other  $\alpha$ -dioxime ligands. We believe the reason for this coordination is the bicyclic nature of the ligand which causes the C-C-C angles at C-12, C-13,