

## Structure of Carbanions having Carbocations as Counterions

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The first X-ray structural analysis of a carbanion having a carbocation as the counterion,  $[\text{EtC}(\text{CO}_2\text{Me})_2]^- \text{C}[(\text{NMe}_2)_3]^+$  is reported, showing unusual hydrogen bonding between the carbanion and the methyl groups of the carbocation.

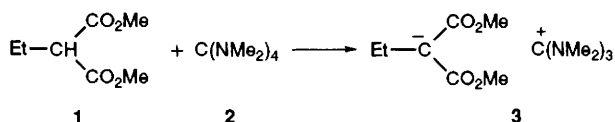
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Carbanions usually react spontaneously with carbocations, C–C bond formation occurring *via* ionic or single electron-transfer processes.<sup>1</sup> However, if both species are resonance-stabilized, carbanions, carbocations and the corresponding free radicals may exist in equilibrium.<sup>2</sup> In fact, this has been used as the basis for the construction of an ‘all-organic’

battery.<sup>3</sup> In the case of highly resonance-stabilized carbanions having well-stabilized carbocations as counterions, electron transfer is likely to be energetically less favourable. Indeed, the reaction of tetrakis(dimethylamino) methane  $\text{C}(\text{NMe}_2)_4$  with highly CH-acidic compounds [malonic acid ester and 1,1-bis-(tolylsulfonyl)methane] has been reported to afford

**Table 1** Pertinent structural parameters of the anionic portion of the salt **3**

Distance/pm	Angle/°		
C(1)–C(2)	151.0(6)	C(2)–C(1)–C(4)	120.5(3)
C(1)–C(4)	141.3(6)	C(2)–C(1)–C(6)	115.6(4)
C(1)–C(6)	141.2(5)	C(4)–C(1)–C(6)	123.3(3)
C(4)–O(3)	122.9(5)	O(1)–C(4)–O(3)	117.7(5)
C(4)–O(1)	140.7(4)	O(1)–C(4)–C(1)	110.9(3)
		O(3)–C(4)–C(1)	131.4(4)
C(6)–O(4)	123.3(5)	O(2)–C(6)–O(4)	118.6(3)
C(6)–O(2)	138.2(4)	O(2)–C(6)–C(1)	115.8(4)
		O(4)–C(6)–C(1)	125.7(3)



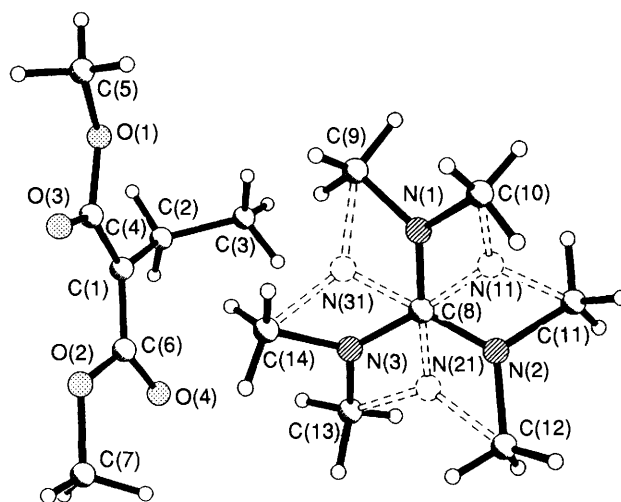
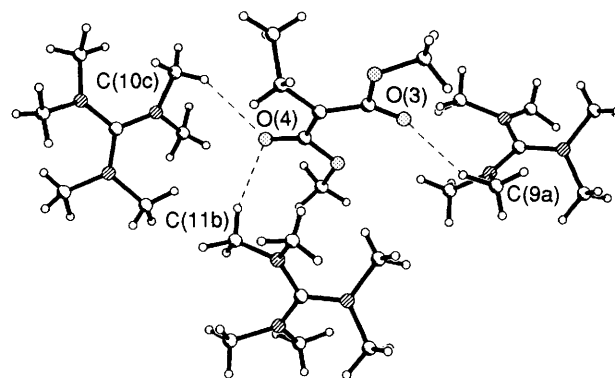
the corresponding hexamethylguanidinium carbanions.<sup>4</sup> However, precise structural data are lacking. We have previously used such carbanions as initiators in the anionic polymerization of acrylates at room temperature.<sup>5</sup> We now report, *inter alia*, the first X-ray structural analysis of a carbanion having a carbocation as the counterion.

Upon adding ethyl malonic acid dimethyl ester **1** to a diethyl ether solution of tetrakis(dimethylamino)methane **2**, the salt **3** is obtained in >90% yield.<sup>6†</sup>

A portion was recrystallized from *N*-methylpyrrolidone/diethyl ether and subjected to an X-ray structural analysis at –120 °C (Fig. 1).‡ In contrast to the usual U-shaped metal chelates of 1,3-dicarbonyl compounds, the enolate has an *s-trans* geometry, *i.e.* the two negatively charged enolate O-atoms are *trans* to one another. In the unit cell there are eight discrete anions and cations (alternating). The most important geometric parameters of the carbanion portion are summarized in Table 1. The carbocation C<sup>+</sup>(NMe<sub>2</sub>)<sub>3</sub> is propeller-shaped with an sp<sup>2</sup>-hybridized central C-atom and disordered in that way that the minor part (15%) can be derived from the main part through a rotation of 60° in the plane of the nitrogen atoms. The methyl groups of both portions are on the same positions, the hydrogens of the main part could be found and have been refined. Relevant is the crystal structure of [Fe(CO)<sub>4</sub>C(O)NMe<sub>2</sub>]<sup>–</sup>[C(NMe<sub>2</sub>)<sub>3</sub>]<sup>+</sup>

† *Procedure*: To a stirred solution of tetrakis(dimethylamino)methane **2** (1.13 g, 6 mmol) in dry diethyl ether is added ethyl malonic acid dimethyl ester (0.96 g, 6 mmol) under an inert gas atmosphere at room temp. After a short time the mixture turns milky and after 12 h the salt **3** precipitates completely. It is filtered, washed twice with 20 ml of light petroleum (b.p. 40/60 °C) and dried *in vacuo* to provide pure hexamethylguanidinium dimethyl-2-ethylmalonate **3** (*ca.* 1.67 g, 92%) as very small needles. In order to grow larger crystals, a portion is dissolved in a small amount of *N*-methylpyrrolidone, and diethyl ether is carefully added to form a layer. Crystals for an X-ray structural analysis are readily obtained.

‡ *Crystal data* for **3**: C<sub>14</sub>H<sub>29</sub>N<sub>3</sub>O<sub>4</sub>; orthorhombic; space group *Pbca*, *a* = 14.715(1), *b* = 15.430(1), *c* = 15.029(1) Å, *Z* = 8; data collection on an Enraf-Nonius CAD4-diffractometer using Cu-Kα radiation, *T* = 183 K, 2933 reflections, 2133 unique (*R*<sub>int</sub> = 0.0713), 1764 observed [*F* > 4σ(*F*)]. Solution with direct methods and full-matrix least-squares refinement with the Siemens SHELXTL PLUS (VMS)-package, non-hydrogen atoms anisotropic, hydrogens of the anion and of the main part of the disordered cation located and isotropically refined, *R* = 0.0676, *wR* = 0.0566 [*w* = 1/σ<sup>2</sup>(*F*)], 321 parameters. Program used: SHELXTL-PLUS (VMS) Vers. 4.2, Siemens Analytical X-Ray Instruments Inc., and Platon-92, A. L. Spek, Univ. Utrecht, 1992. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

**Fig. 1** Asymmetric unit of the crystal structure of **3****Fig. 2** Hydrogen bonds between the anion and neighbouring carbocations in the salt **3**

reported by Petz *et al.*,<sup>7</sup> which also contains a propeller-shaped guanidinium cation. Fig. 1 shows the asymmetric unit of the crystal structure of **3**.

Another structural feature concerns the interaction between carbanion and carbocations. The negatively charged *s-trans* O-atoms participate in hydrogen bonding with H-atoms of methyl groups in the hexamethylguanidinium ions, forming a self-organized network. Fig. 2 shows the closest contacts of the anion to neighbouring carbocations.

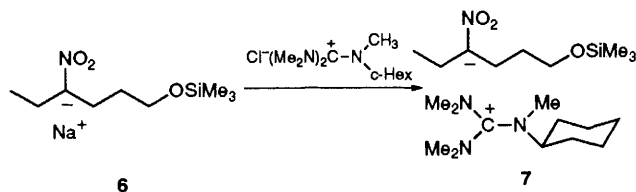
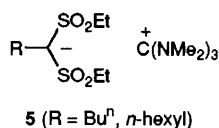
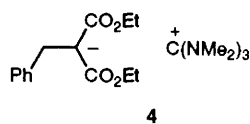
Hydrogen bonding based on the interaction of H-atoms of methyl groups with lone pairs of an acceptor A (R–Me⋯A) are known to be weak.<sup>8</sup> It is likely that the positive charge of the cation facilitates this interesting interaction. Thus, the metal-free anion in **3** is not a real 'naked' carbanion in the solid state.

It was possible to obtain a correct elemental analysis<sup>6</sup> of compound **3**, as well as NMR data: H NMR (300 MHz, (CD<sub>3</sub>)<sub>2</sub>SO): δ 0.82 (t, *J* 7.1 Hz; 3H, CH<sub>3</sub>), 2.12 (q, *J* 7.1 Hz; 2H, CH<sub>2</sub>), 2.93 (s, 18H, NMe<sub>2</sub>), 3.31 (s, 6H, OCH<sub>3</sub>). <sup>13</sup>C NMR [75 MHz, (CD<sub>3</sub>)<sub>2</sub>SO]: δ 16.34, 20.94, 39.13 (NMe<sub>2</sub>), 47.62, 72.53, 162.23 (cation C<sup>+</sup>), 168.0. The <sup>13</sup>C NMR signal for the carbonyl C-atom at δ 168 is broad at room temp., but sharp at 80 °C. This is due to 'equilibration' of the two carbonyl C-atoms *via* rotation about the C–C bond in the enolate anion.

Using the same synthetic procedure, the diethyl ester analogue of **3** was prepared, as well as compounds **4–5** which were all characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. Accordingly, they are all ionic as shown by the characteristic sharp <sup>13</sup>C NMR signal at δ 162.2 to 162.4 for the central

**Table 2** Parameters of the hydrogen bonds between the anion and carbocations in the salt **3**

Distance/pm	C...O	H...O		Angle/° C-H...O
C(9a)...O(3)	324.6(7)	H(9c)...O(3)	231(4)	C(9a)-H(9c)...O(3) 142(3)
C(10c)...O(4)	334.0(5)	H(10b)...O(4)	249(4)	C(10c)-H(10b)...O(4) 148(4)
C(11b)...O(4)	326.1(6)	H(11a)...O(4)	240(4)	C(11b)-H(11a)...O(4) 153(4)



C-atom of the guanidinium cation  $C^+(NMe_2)_3$ . Thus, covalent bonding between carbanion and carbocation, *e.g.* via C–O bonds, can definitely be ruled out. Compounds **3–5** can also be prepared by treating the corresponding Na-salt with  $Cl^-(NMe_2)_2C^+(CH_3)-N^{c-Hex}$  in tetrahydrofuran (THF) and separating from the precipitated NaCl (salt method).

The salt method was also used in the synthesis of the nitro carbanion **7**. In this case the cyclohexylpentamethylguanidinium counterion was used in order to increase solubility in organic solvents. All of the salts induce the anionic polymerization of *n*-butyl acrylate at room temp.<sup>6</sup>

In summary, we have provided for the first time conclusive structural data for carbanions having carbocations as counterions. We are currently studying their synthetic utility as well as photoinduced electron-transfer processes.

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