# Tetrabutylammonium Salts of Carbazole and Dibenzoazepine: Synthesis, Crystal Structures and Use in Anionic Polymerization

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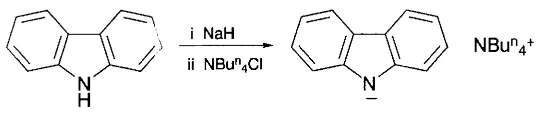
X-Ray structure analyses of the easily accessible tetrabutylammonium salts of carbazole and dibenzoazepine indicate that the anions and cations interact with one another *via* hydrogen bonding; these nitrogen nucleophiles initiate the anionic polymerization of acrylates and methacrylates at room temperature.

Metal-free anionic polymerization of $\alpha$-activated olefins such as acrylates, methacrylates and acrylonitrile using carbanionic initiators with tetraalkylammonium counterions[1] is an alternative to other recent developments in the field.[2] We have described the syntheses and crystal structures of several tetraalkylammonium salts of CH-acidic compounds such as malonic acid esters,[1,3] phenylacetic acid ester[4] or nitropropane[5] and their use as initiators in the anionic polymerization of $\alpha$-activated olefins at room temperature. Since such carbon nucleophiles have also been postulated as reactive intermediates in phase-transfer catalysed alkylation reactions[6] and in other C–C bond forming processes,[7] their structure is of considerable interest. They are not 'naked' carbanions as traditionally postulated,[6,7] but the $\alpha$-methylene groups of the ammonium ions form hydrogen bonds to the negatively charged O-atoms of enolates[3,4] or nitronates,[5] in some cases with formation of supramolecular dimeric species in the solid state and in solution. We now report that certain anionic *nitrogen* nucleophiles with tetraalkylammonium counterions are similarly useful polymerization initiators, and that such salts are also stabilized by hydrogen bonding.



**1** **2**

Deprotonation of carbazole **1** with NaH in THF and reaction of the sodium salt with $NBu^n_4Cl$ yielded the yellow hygroscopic salt **2**.† The $^1H$ and $^{13}C$ NMR spectra of the crude product indicate high purity.[8] The compound is stable at room temperature for weeks under an inert gas atmosphere. Under the influence of UV light it shows blue fluorescence.[8,9] Slow recrystallization from dimethylformamide at −60 °C afforded crystals suitable for an X-ray structural analysis.‡

The results (Fig. 1) indicate that, in spite of being an aromatic Hückel species, the carbazolide anion is stabilized by weak $[CH\cdots N]^-$ bonds involving the $\alpha$-methylene entities of the ammonium counterion and the basic N-atom of the heterocycle. Interestingly, this interaction occurs mainly with one ammonium ion, as evidenced by the relatively short C(1*)···N(2) contact of 3.339(7) Å. A similar contact on the other side of the $\pi$ plane of the heterocycle is longer [C(9)···N(2) 3.674(7) Å]. These distances may be compared with the closest contact between the anion and cation of 3.492(4) Å [C–H···C] in the crystal structure of $NBu^n_4(C_5H_5)$ or 3.373(2) Å in that of tetra-*n*-butylammonium-9-ethylfluorenide where we attributed little or no hydrogen-bonding.[5] In **2**, however, one of the calculated H atoms on each of the $\alpha$-methylene groups of the tetrabutylammonium cations at C(1) and C(9) points directly towards the carbazolide N atom. Apart from one short contact C(1)···C(17) of 3.394(8) Å, there is no appreciable interaction of the $NBu^n_4{}^+$ ions with the remaining C atoms of the anionic $\pi$-system (C···C > 3.5 Å), which means that the structure is different from those of the multihapto-bound $Li^+$, $Na^+$, $K^+$ and $Cs^+$ analogues.[10] The solid-state structure of **2** can thus be considered as consisting of polymeric chains; these lie parallel in the crystal and are close packed.

The synthesis of the tetrabutylammonium salt **4** from dibenzoazepine **3** was effected by simple deprotonation using commercially available $NBu^n_4OH$ in methanol. Following azeotropic removal of water by toluene,[1,3] compound **4** was isolated in 85% yield as a dark green hygroscopic salt.§ Within

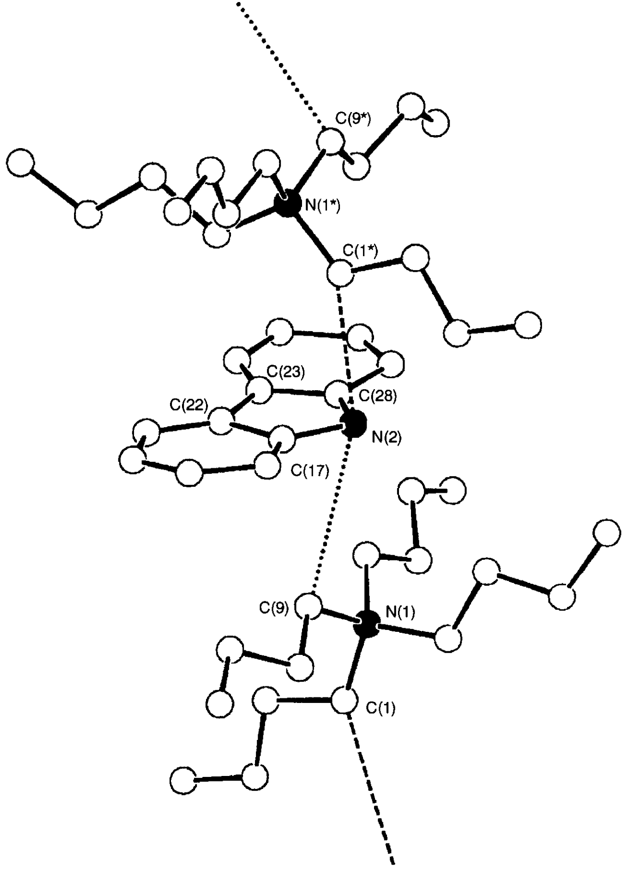
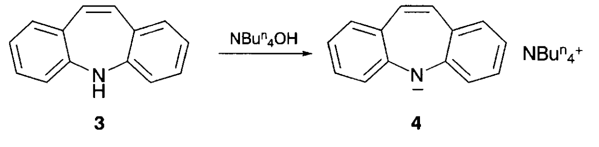


**Fig. 1** Structure of **2** in the crystal, showing the environment of the carbazolide anion (symmetry related atoms denoted by *). H-atoms omitted for clarity. Selected interatomic distances (Å) and angles (°): N(2)···C(1*) 3.339(7), N(2)···C(9) 3.674(7), N(2)–C(17) 1.34(1), N(2)–C(28) 1.29(1), C(17)–C(22) 1.38(1), C(28)–C(23) 1.38(2), C(22)–C(23) 1.43(1), C(17)–N(2)···C(1*) 80.8(4), C(28)–N(2)···C(1*) 104.6(4), C(17)–N(2)···C(9) 80.6(4), C(28)–N(2)···C(9) 82.3(4), C(1*)···N(2)···C(9) 161.3(3), C(17)–N(2)–C(28) 103.9(7), N(2)–C(28)–C(23) 115.2(9), N(2)–C(17)–C(22) 113.9(7), C(17)–C(22)–C(23) 103.1(8), C(22)–C(23)–C(28) 103.9(7).



**3** **4**

the context of Hückel's theory of aromaticity, it is expected to have antiaromatic character. $^1H$ and $^{13}C$ NMR data are in accord with the proposed structure.[8] A sample was dissolved in DMF and placed in a cooling bath at −60 °C for three days, affording crystals suitable for an X-ray analysis.‡ The crystal structure is similar to that of the salt **2** in that the α-methylene groups of the tetrabutylammonium ions form hydrogen bonds to the nitrogen atom of the negatively charged heterocycle (Fig. 2). These contacts occur both above and below the anion and are approximately equal [C(1)···N(2) 3.350(6) and C(13*)···N(2) 3.371(6) Å]. In contrast to **2**, the cations approach from outside the central ring, thus completing a distorted tetrahedral coordination about the negatively charged N-atom.

The seven-membered ring in **4** has a non-planar butterfly-form, similar to that of dibenzoazepine.[11] However, the degree of puckering is less pronounced, *i.e.* it is on the way to planarity, and the angle between the two halves of the molecule defined by the mirror plane is 144.4(1)° for dibenzoazepine[11] and 161(1)° for the anion in **2**, consistent with a rehybridization of the N atom. The limited solubility of salts **2** and **4** did not permit a cryoscopic study in benzene. However, it is likely that hydrogen-bonding between anion and cation also pertains in solution, regardless of the aggregation state. This may be relevant for the phase-transfer catalysed alkylations of heterocycles of types **1** and **3**.[6]

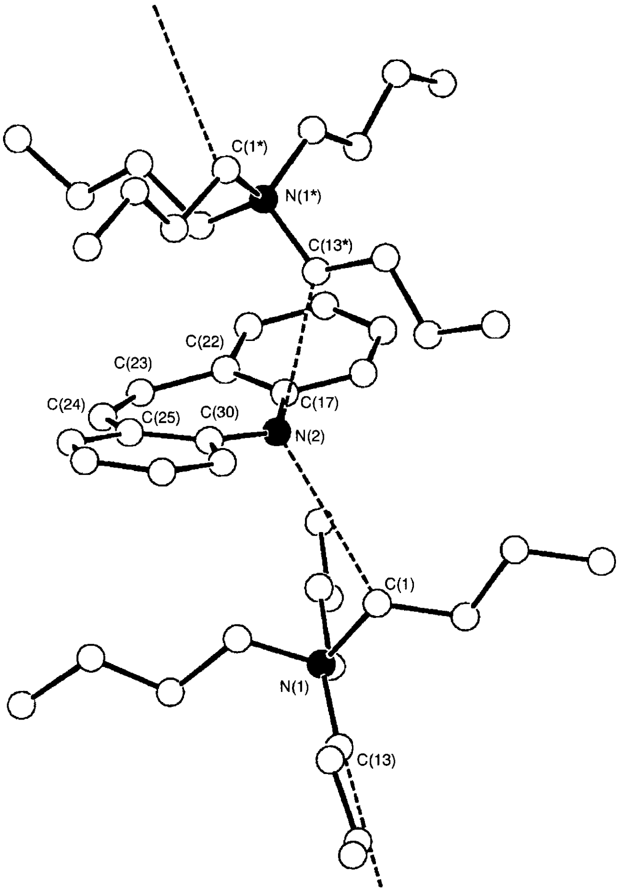


**Fig. 2** Structure of **4** in the crystal, showing the environment of the dibenzoazepide anion (symmetry related atoms denoted by *). H-atoms omitted for clarity. Selected interatomic distances (Å) and angles (°): N(2)···C(1) 3.350(6), N(2)···C(13*) 3.371(6), N(2)–C(17) 1.359(8), N(2)–C(30) 1.36(1), C(17)–C(22) 1.423(9), C(30)–C(25) 1.39(1), C(22)–C(23) 1.48(1), C(24)–C(25) 1.41(2), C(23)–C(24) 1.32(1), C(17)–N(2)···C(13*) 95.3(3), C(30)–N(2)···C(13*) 85.8(3), C(17)–N(2)···C(1) 116.3(3), C(30)–N(2)···C(1) 106.7(3), C(1)···N(2)···C(13*) 122.8(2), C(17)–N(2)–C(30) 126.8(6), C(22)–C(17)–N(2) 130.5(6), C(25)–C(30)–N(2) 131.5(7), C(17)–C(22)–C(23) 122.1(6), C(24)–C(25)–C(30) 123.1(8), C(22)–C(23)–C(24) 128.1(7), C(23)–C(24)–C(25) 132.3(9).

The two salts were tested as initiators for the anionic polymerization of *n*-butyl acrylate (BA) and methyl methacrylate (MMA). In doing so, monomer was added to a solution of the initiator in THF under an atmosphere of an inert gas at 22–35 °C as previously described for metal-free polymerizations using C-nucleophiles.[1,4,5] In all cases an exothermic reaction was observed with formation of PBA and PMMA in yields of 65–100%. In the case of BA, narrow molecular weight distributions ($D = M_n/M_w$) of 1.1–1.4 were obtained, particularly when aiming for low molecular weight polymers.[9] Typical data for **2**: $M_n$(calc.) = 2770; $M_n$(exptl.) = 2270; $D$ = 1.37 (95% yield); $M_n$(calc.) = 6300; $M_n$(exptl.) = 2900; $D$ = 1.45 (75% yield). Typical data for **4**: $M_n$(calc.) = 3220; $M_n$(exptl.) = 1910; $D$ = 1.22 (91% yield). In the case of the less reactive MMA, an induction period of 1–3 min was observed, and $M_n$(exptl.) consistently turned out to be considerably higher than $M_n$(calc.). Comparing these metal-free polymerizations with those initiated by malonates[1,3] or nitronates,[5] it is found that broader molecular weight distributions result in some cases, although optimization has not been carried out. Typical data for **2**: $M_n$(calc.) = 3160; $M_n$(exptl.) = 20490; $D$ = 1.49 (100% yield). Typical data for **4**: $M_n$(calc.) = 3600; $M_n$(exptl.) = 16940; $D$ = 1.68 (90% yield). It is important to point out that the products are functionalized polymers with specific heterocyclic end groups, and that the method of polymerization may be industrially viable because the initiators are cheap and low temperatures are avoided. Other metal-free nitrogen anions derived from NH-acidic compounds are currently being studied in our laboratories.

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## Footnotes

† *Synthesis of* **2**: a solution of the sodium salt of carbazole (20 mmol) in 20 ml of dry THF, prepared by reacting **1** with NaH, was added to a suspension of tetrabutylammonium chloride (20 mmol) in 30 ml of THF under an inert gas atmosphere. After stirring for 3 h, NaCl was filtered off and the solvent removed *in vacuo*, providing 7.8 g (95%) of salt **2**.

‡ *Crystal data*: **2**, $C_{28}H_{44}N_2$, $M$ = 408.7, yellow, crystal size 0.25 × 0.49 × 0.42 mm, $a$ = 9.784(1), $b$ = 16.274(1), $c$ = 16.734(1) Å, β = 97.33(1)°, $V$ = 2642.7(2) Å$^3$, $T$ = 293 K, $D_c$ = 1.03 g cm$^{-3}$. μ = 4.11 cm$^{-1}$, $F(000)$ = 904, $Z$ = 4, monoclinic, space group $P2_1/n$ [no. 14], Enraf-Nonius CAD4 diffractometer, λ = 1.54178 Å, measuring method ω–2θ, 11521 measured reflections ($\pm h, \pm k, +l$), $[(\sin\theta)/\lambda]_{max}$ = 0.63 Å$^{-1}$, 5439 independent reflections, 2515 observed reflections [$I \geqslant 2\sigma(I)$] for 271 refined parameters, structure solved by direct methods, non-hydrogen atoms refined anisotropically, H-atom positions calculated and fixed ($U_H$ = 0.05 Å$^2$) in the final refinement stages, $\Sigma w(F_o - F_c)^2$ minimised, $R$ = 0.111, $R_w$ = 0.127 [$w = 1/\sigma^2(F_o)$], max. shift/error 0.12, final difference Fourier ρ = 0.30 e Å$^{-3}$.

**4**, $C_{30}H_{46}N_2$, $M$ = 434.7, dark green, crystal size 0.46 × 0.46 × 0.63 mm, $a$ = 9.784(2), $b$ = 18.205(7), $c$ = 16.177(3) Å, β = 104.07(1)°, $V$ = 2795(1) Å$^3$, $T$ = 293 K, $D_c$ = 1.03 g cm$^{-3}$, μ = 0.55 cm$^{-1}$, $F(000)$ = 960, $Z$ = 4, monoclinic, space group $P2_1/c$ [no. 14], Enraf-Nonius CAD4 diffractometer, λ = 0.71069 Å, measuring method ω-2θ, 6803 measured reflections ($\pm h, +k, +l$), $[(\sin\theta)/\lambda]_{max}$ 0.65 Å$^{-1}$, 6367 independent reflections, 2707 observed reflections [$I \geqslant 2\sigma(I)$] for 289 refined parameters, structure solved by direct methods, non-hydrogen atoms refined anisotropically, H-atom positions calculated and fixed ($U_H$ = 0.05 Å$^2$) in the final refinement stages, $\Sigma w(F_o - F_c)^2$ minimised, $R$ = 0.096, $R_w$ = 0.107 [$w = 1/\sigma^2(F_o)$], max. shift/error 0.04, final difference Fourier ρ = 0.21 e Å$^{-3}$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ *Synthesis of* **4**: a mixture of 20 mmol of dibenzoazepine **3** and 20 ml (20 mmol) of tetrabutylammonium hydroxide in methanol (1 mol dm$^{-3}$) was stirred for 5 min. The solvent was removed *in vacuo* and the residue dried under high vacuum conditions in the presence of $P_4O_{10}$, providing 7.4 g (85%) of salt **4**.

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