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Salts and Ionic Liquids of Resonance Stabilized Amides

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Abstract: The synthesis, structure, and bonding of alkali salts of resonance stabilized amides, such as diformylamide (dfa), formylcyanoamide (fca), nitrocyanoamide (nca), and for comparision, the well-known dicyanoamide (dca), are discussed on the basis of experimental and theoretical data. The first structural reports of K(18-crown-6)$^+$ dfa$^-$, K(18-crown-6)$^+$fca$^-$, Na$^+$nca$^-$, and Li(TMEDA)$^+$dca$^-$ are presented. Examination of the X-ray data reveals almost planar anions with strong cation–anion interactions resulting in network-like structures in the solid state. For comparison, the X-ray structures of covalently bound phenyldicyanoamide and diformamide are also discussed. The thermal behavior of the alkali salts of these amides is studied by thermoanalytical experiments. Moreover, several novel ionic liquids based on resonance stabilized amides have been prepared and were fully characterized, namely the dfa, fca, and nca salts of EMIM (1-ethyl-3-methyl-imidazolium), BMIM (1-butyl-3-methyl-imidazolium), and HMIM (1-hexyl-3-methyl-imidazolium). Most of them are liquid at room temperature, except BMIM$^+$fca$^-$ that melts at 32 °C. These ionic liquids are neither heat nor shock sensitive, are thermally stable up to over 200 °C, and can be prepared easily in large quantities.

Keywords: amides · density functional calculations · ionic liquids · halides · Raman spectroscopy

Introduction

Amides of the type $[NR^1R^2]^-$ with $R^{1,2}$ = CHO, NO_2, CN, being an electron withdrawing group, can be regarded as nonlinear resonance stabilized pseudohalides.[1] Although salts of dicyanoamides are well-studied, much less is known about formylamide, formylcyanoamide, and nitrocyanoamide salts.[2]

The first alkali diformylamide compound was reported by Allenstein and Beyl in 1967.[3] In contrast to the experimentally unknown acid of dca, $HN(CN)_2$, the free acid of dfa, $HN(CHO)_2$, has been synthesized and identified on the basis of IR, microwave, and ^{1}H NMR data.[3–5] As expected for a pseudohalide, the silver salt is insoluble in water,[6] and it was possible to isolate the very labile halogen–pseudohalogen compound bromodiformylamide, $BrN(CHO)_2$, in small yields.[3] Tetraformylhydrazine represents, according to the pseudohalogen concept, a bimolecular pseudohalogen which is known and fully characterized.[7] Sodium diformylamide is easily prepared by treatment of sodium methanolate with formamide at elevated temperatures [Eq. (1)]:[8]

$$NaOCH_3 + 2\,H_2NCHO \rightarrow Na[N(CHO)_2] + NH_3 + H_3COH \quad (1)$$

Sodium formylcyanoamide has been synthesized from sodium hydrogencyanoamide and ethyl formate according to Equation (2).[9] However, detailed spectroscopic data of alkali formylcyanoamides is still required.

$$Na[HNCN] + H_5C_2OCHO \rightarrow Na[N(CHO)CN] + H_5C_2OH \quad (2)$$

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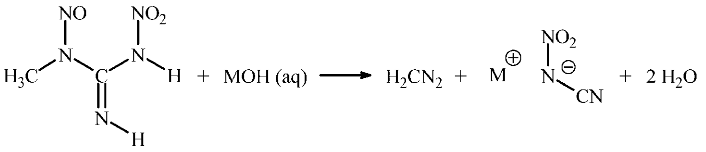
Besides the application of sodium and potassium formylcyanoamide as precursors in heterocycle synthesis,[10] as well as in some theoretical works on the free formylcyanoamide,[11] inorganic covalently bound formylcyanoamides have not yet been discussed in detail. However, the 3,4-dichlorophenyl[12] and the methylformylcyanoamide can be found in the literature.[13]

Analogous to the formylcyanoamides, alkali dicyanoamides are also nonlinear pseudohalides with one lone pair of the central nitrogen atom strongly delocalized into the two π*(C−N) bonds. Sodium dicyanoamide has been synthesized as early as 1922 by Madelung and Kern.[14] Typically for a pseudohalide, the heavy metal salts (Ag^+, Hg_2^{2+}, Pb^{2+}) are sparingly soluble in water.[14–16] Neither the free acid nor any halogen–pseudohalogen species has been isolated so far. Interestingly, Madelung and Kern have already observed the trimerization of sodium dicyanoamide at “dark red heat”.[17a] In the last decade, this trimerization process leading to promising melaminate salts has been the object of great interest by several groups.[17,18] In addition, the synthesis and structural investigations of a series of hitherto unknown dca salts (earth alkali,[19] ammonium,[20] guanidinium,[21] rare earth,[22] and guanylurea[23]) have been reported recently.

McKay and co-workers were the first group able to isolate the explosive potassium nitrocyanoamide as they studied the properties of *N*-alkyl-*N*-nitroso-*N*′-nitroguanidines.[24] For instance, treatment of *N*-methyl-*N*-nitroso-*N*′-nitroguanidine with MOH (M = alkali metal) yields, beside diazomethane, the alkali nitrocyanoamide $M[N(NO_2)CN]$ [Eq. (3)].[25]



(3)

Another synthetic route starts from *S*-methyl-*N*-nitroisothiourea,[26] which can be converted to $M[N(NO_2)CN]$ in basic solutions of MOH.[27] Nitrocyanoamide salts have been studied as potential primary explosives.[28]

Since ionic liquids are increasingly receiving more attention owing to their wide spectrum of applications (as reaction media, as lubricants, or as electrolytes particularly for solar and fuel cells),[29–37] the EMIM (1-ethyl-3-methyl-imidazolium), BMIM (1-butyl-3-methyl-imidazolium), and HMIM (1-hexyl-3-methyl-imidazolium) salts of dfa, fca, and nca have also been prepared and fully characterized.

Results and Discussion

Synthesis, Properties, and Structure of Diformamide, $HN(CHO)_2$

According to Allenstein and Beyl, the addition of HCl gas dissolved in diethyl ether to a suspension of sodium diformylamide in diethyl ether at 0 °C gives $HN(CHO)_2$ (Hdfa) in good yields.[3] For practical reasons we have passed HCl gas directly into a stirred suspension of sodium diformylamide [Eq. (4)].

$$Na[N(CHO)_2] + HCl\ (g) \rightarrow HN(CHO)_2 + NaCl \qquad (4)$$

The ^1H NMR spectrum of Hdfa shows two resonances in the typical range of dicarbon acid imides (11.16 ppm, *cf.* 11.40 ppm for phthalimide $H_4C_6(CO)_2NH$)[38] and formamides (8.83 ppm, *cf.* 8.00 ppm for (*Z*)-*N*-methylformamide (*Z*)-MeN(H)C*H*O), respectively.[39] As expected, a singlet is found in the ^{13}C NMR spectrum (167.2 ppm, *cf.* 163.6 ppm for H_2NCHO)[39] and ^{14}N NMR spectrum (−207 ppm, *cf.* −199 ppm for succinimide $(H_2C)_2(CO)_2NH$).[40] On the basis of B3LYP/6-31G(d,p) computations, the experimentally obtained vibrational frequencies of Hdfa were assigned to the corresponding vibrations (Table 1).

Hdfa is hygroscopic and should be kept in a dry argon atmosphere. DSC studies revealed a melting point of 44 °C (*cf.* 42 °C)[3] and a boiling point of 198 °C at atmospheric pressure (*cf.* 119 °C at 12 Torr [16 mbar]),[3] indicating an astonishing thermal stability in contrast to the other free acids of nonlinear pseudohalides.[1]

Three conformers (*E,E*; *Z,E;* and *Z,Z*) of Hdca have been found at the potential energy surface (Figure 1), with the *E,E*-conformer being the most stable isomer followed by the *Z,E*-isomer (+0.2 kcal mol^{-1}) and the *Z,Z*-conformer (+6.0 kcal mol^{-1}). Obviously, this trend can be attributed to the decreasing number of formal intramolecular hydrogen bonds (*E,E:* 2; *Z,E:* 1; and *Z,Z:* 0 hydrogen bonds). A better explanation might be the fact that *E,E*-conformer of Hdfa avoids the destabilizing 1,3-interactions in contrast to the *E,Z* and *Z,Z* form. This finding is in contradiction to a microwave study by Steinmetz (in 1973) who concluded from the experimental data that the (*Z,E*)-diformamide should be favored energetically.[4] Two years later, Noe and Raban reported (*E,E*)-diformamide on the basis of ^1H NMR data as the most stable conformer.[5] To shed some light on this structural problem, a single crystal X-ray study was carried out.

X-ray Study of Hdfa

Single crystals of Hdfa suitable for X-ray structure analysis were obtained from recrystallization in diethyl ether. Hdfa crystallizes in the orthorhombic space group $Pca2_1$ with four molecules per unit (Table 2). In agreement with the computed results the Hdfa molecule exhibits an (*E,E*)-conformation (Figure 1 and 2). The O1-C1-N1-C2 and C1-N1-C2-O2 dihedral angles amount to 179.4° and −179.4°, respectively. Thus the Hdfa molecule can be regarded as a planar C_{2v} symmetric species. Selected structural data are listed in Figure 2. The computed and experimentally observed data are in good agreement (for comparison see Table S1 in the Supporting Information). The O1–C1 and O2–C2 distances

Table 1. Calculated and experimental vibrational data of Hdfa (cm^{-1}) along with an approximate assignement.[a]

assignment[b]	B3LYP/6-31G(d,p)[c]	Hdfa Raman[d]	IR[e]
ν_{N-H}	3584(75,46)	3256(1)	3262 s
$\nu_{s,C-H}$	3002(137,113)	2955(2)	2917 m
$\nu_{as,C-H}$	2982(4,0)	2934(1)	2898 sh
$\nu_{s,C=O}$	1858(48,22)	1739/1719(10)	1745 s
$\nu_{as,C=O}$	1825(1,746)	–	1686 vs
$\delta_{as,N-H/C-H}$ ($\delta_{s,C-H}$)	1478(6,20)	1450(1)	1480 m
$\delta_{as,C-H}$	1450(5,1)	1431(5)	1412 w
$\delta_{s,N-H/C-H}$ ($\delta_{s,C-H}$)	1348(2,29)	1372/1359(0.4)	1373/1347 m
$\nu_{s,C-N}$	1256(3,62)	1264(1)	1264 m
$\nu_{as,C-N}$	1185(2,290)	1192/1167(0.4)	1188 s
$\gamma_{s,C-H}$	1044(4,1)	1090/1077(0.5)	1088/1041 w
$\gamma_{as,C-H}$	1031(1,0)	1038(0.3)	–
γ_{N-H}	742(1,137)	769(0.3)	796 m
$\delta_{as,NCO}$	629(0,51)	–	649 s
$\delta_{s,NCO}$	533(9,0)	547(9)	527 m
$\delta_{OHC-N(H)-CHO,bending}$	248(1,28)	231(1)	–

[a] Data correspond to the (*E*,*E*)-conformer of Hdfa. [b] s = symmetric and as = antisymmetric mode. [c] Unscaled calculated frequencies; in round brackets: IR intensities ($km\,mol^{-1}$), Raman activities ($Å^4\,amu^{-1}$). [d] Experimental Raman intensity scaled to the maximum value 10. [e] KBr pellet.

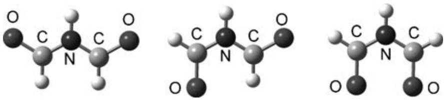


Figure 1. Computed conformers of Hdfa.

are 1.206 Å and 1.209 Å, respectively, in accord with the calculated value of 1.209 Å. The N1−C1 and the N1−C2 bond lengths of 1.374 Å and 1.356 Å correspond to a partial double bond character (*cf.* d_{cov}(C=N) = 1.270 Å; d_{cov}(C−N) = 1.470 Å).[41] As expected the N1-C1-H2 and N1-C1-H2 angles are significantly smaller compared to the C1-N1-C2 angle of 122.5° (Figure 1).

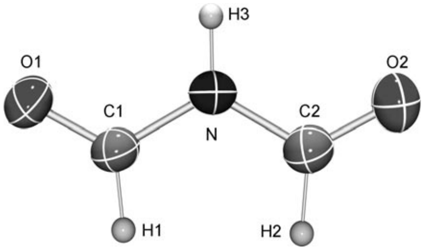


Figure 2. ORTEP drawing of the molecular structure of Hdfa in the crystal. Thermal ellipsoids with 50 % probability at 200 K. Selected bond lengths [Å] and angles [°]: O1−C1 1.206(3), N−C2 1.356(3), O2−C2 1.209(2), N−C1 1.374(3); C1-*N*-C2 122.5(2), O1-C1-N 124.0(2), O2-C2-H3 121.1(16), C1-*N*-H3 117.0(20), O2-C2-N 124.6(2), N-C1-H2 112.6(14), C2-*N*-H3 120.0(20), O1-C1-H2 123.2(14), N-C2-H3 114.1(16).

A number of inter- and intramolecular hydrogen bonds ranging from 2.2 to 2.9 Å are observed (Figure 3). Moreover, the hdfa molecules are arranged in two planes, which are almost perpendicular to each other. The very good thermal stability can be attributed directly to the large number of strong hydrogen bonds.

The electronic structure is best represented by the resonance between the three Lewis structures shown in Figure 4, indicating a partial CN double bond through the delocalization of the nitrogen lone pair into CO π* orbitals.

Table 2. Crystallographic data.[a]

	Hdfa	K(18-crown-6)$^+$dfa$^-$	K(18-crown-6)$^+$fca$^-$	Phdca	Na$^+$nca$^-$
formula	$C_2H_3NO_2$	$C_{14}H_{26}KNO_8$	$C_{14}H_{25}KN_2O_7$	$C_8H_5N_3$	CN_3NaO_2
M	73.05	375.46	372.46	143.15	109.02
crystal system	orthorhombic	orthorhombic	monoclinic	monoclinic	monoclinic
space group	$Pca2_1$	$P2_12_12_1$	Pc	$P2_1/c$	$P2_1/n$
a [Å]	8.0885(3)	8.190(7)	8.2266(13)	7.4864(7)	3.5888(4)
b [Å]	4.7789(2)	10.764(5)	14.314(2)	6.0980(4)	15.414(2)
c [Å]	8.2554(3)	21.173(8)	8.1294(14)	15.5461(16)	6.7803(7)
α [°]	90	90	90.00	90.00	90.00
β [°]	90	90	99.629(14)	94.556(4)	101.035(13)
γ [°]	90	90	90.00	90.00	90.00
V [$Å^3$]	319.11(2)	1866.6(19)	943.8(3)	707.47(11)	368.14(8)
Z	4	4	2	4	4
$\rho_{calcd.}$ [$g\,cm^{-3}$]	1.521	1.336	1.311	1.344	1.967
μ [mm^{-1}]	0.137	0.323	0.316	0.087	0.273
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
T [K]	200	295	295	200	200
measured refl.	8495	3400	3200	2481	3164
indep. refl.	736	2921	2955	1379	828
R_{int}	0.055	0.0339	0.0108	0.092	0.032
obs. refl.	598	2465	2270	680	683
F(000)	152	800	396	296	216
R_1	0.0378	0.0368	0.0442	0.0545	0.0250
wR_2	0.1038	0.0878	0.1075	0.1153	0.0685
GooF	1.11	1.07	1.11	0.90	1.03
# of parameters	59	217	217	120	64

[a] dfa = diformylamide, fca = formylcyanoamide, dca = dicyanoamide, nca = nitrocyanoamide.

Synthesis, Properties, and Structure of Alkali Diformylamides, M[N(CHO)$_2$]

Alkali diformylamides are easily prepared in an acid/base reaction of Hdfa and MOR (M = alkali metal, R = Me, *t*Bu, and so forth) in THF at 0 °C.[3] The ^{1}H NMR spectrum shows one resonance at 8.95 ppm which lies in the typical range of formamides (*cf.* 8.00 ppm for (*Z*)-*N*-methylformamide (*Z*)-MeN(H)C*H*O).[39] Only a singlet resonance is found in the ^{13}C NMR (181.3 ppm, *cf.* 178.6 ppm in diacetamide anion ($H_3CCO)_2N^-$)[42] and ^{14}N NMR spectrum (−128 ppm, *cf.* −140 ppm for sodium succinimide ($H_2C)_2(CO)_2$*N*Na).[43] IR and Raman data are listed in Table 3.

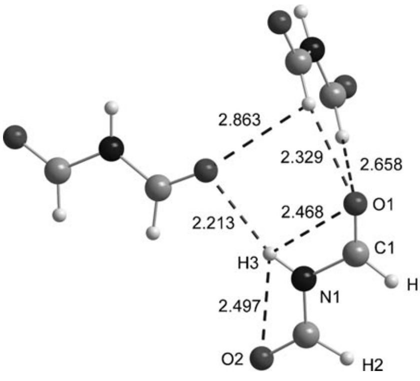


Figure 3. Inter- and intramolecular hydrogen bonds in Hdfa (distances in Å).

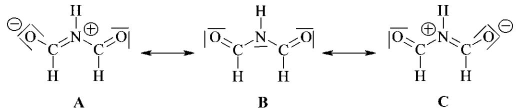


Figure 4. Lewis structures of Hdfa.

Table 3. Experimental and theoretical IR and Raman data (cm^{-1}) of dfa salts along with an approximate assignment.[a]

assignment[b]	B3LYP/ 6-31G(d,p)[c]	Li^+dfa^- Raman[d]	IR[e]	Na^+dfa^- Raman[d]	IR[e]	K^+dfa^- Raman[d]	IR[e]
$\nu_{s,C-H}$	2693(137,508)	2847(1)	2856 w	2862(2)	2833 m	2853(1)	2838 w
$\nu_{as,C-H}$	2633(9,8)	2766(2)	2747 vw	2776(2)	2716 w	2771(2)	2771 w
$\nu_{s,C=O}$	1794(35,36)	1747/1709(10)	1694 vs	1677(10)	1694 s	1668(10)	1698 s
$\nu_{as,C=O}$	1707(0,1240)	–	1604 vs	–	1591 vs	–	1560 vs
$\delta_{as,C-H}$	1463(5,2)	–	1386 s	1422(3)	1388 m	1421(3)	1387 m
$\delta_{s,C-H}$	1441(12,3)	1415(2)	1370 s	1405(1)	1363 s	1409(1)	1349 m
$\nu_{as,C-N}$	1327(5,185)	1313/1308(1)	1287 m	1274(1)	1291 m	1294(1)	1282 s
$\nu_{s,C-N}$	1246(8,137)	1268(1)	1263 m	1261(2)	1264 m	1258(2)	1251 m
$\gamma_{s,C-H}$	1056(7,10)	1048(1)	1055 w	1063(1)	1089 w	1051(1)	1130 w
$\delta_{as,NCO}$	743(0,28)	–	785 m	–	778 m	–	740 m
$\delta_{s,NCO}$	591(16,2)	616(4)	618 m	602(8)	605 m	593(8)	610 m
$\delta_{OHC\text{-}N\text{-}CHO,bending}$	312(2,5)	339(1)	–	320(2)	–	317(2)	–

[a] Data correspond to the (*E*,*E*)-conformer of dfa anion. [b] s = symmetric and as = antisymmetric mode. [c] Unscaled calculated frequencies; in round brackets: IR intensities ($km\,mol^{-1}$), Raman activities ($Å^4\,amu^{-1}$). [d] Experimental Raman intensity scaled to the maximum value 10. [e] KBr pellet.

Alkali diformylamides should be stored under dry nitrogen/argon atmosphere. They are moisture sensitive and decompose rapidly in the presence of water according to Equation (5) (M = alkali metal):

$$M[N(CHO)_2]+H_2O \rightarrow M[HCO_2]+H_2NCHO \qquad (5)$$

DSC experiments on alkali diformylamides of the type ($M[N(CHO)_2]$, M = Li, Na, K) showed that Li^+dfa^- should possess the lowest melting point. However, Li^+dfa^- decomposes at 175 °C (decomposition onset) in an exothermic reaction before reaching the expected melting point. The melting point of Na^+dfa^- was observed at 242 °C, further heating leads to decomposition at 286 °C. A similar result was found for K^+dfa^- (m.p. 237 °C, T_{dec} above 384 °C).

Computations at the B3LYP/6-31G(d,p) level of theory resulted in three possible conformers for the dfa anion (Figure 5) which are all close in energy. The planar C_{2v} symmetric (*E*,*E*)-conformer is energetically favored and stabilized by 2 $kcal\,mol^{-1}$ compared to the non-planar C_1 symmetric (*Z*,*E*)-conformer, as well as 7 $kcal\,mol^{-1}$ with respect to the C_2 symmetric (*Z*,*Z*)-conformer. In the (*E*,*E*)-diformylamide anion, the lone pair density localized at the central nitrogen atom is best delocalized according to Figure 6.

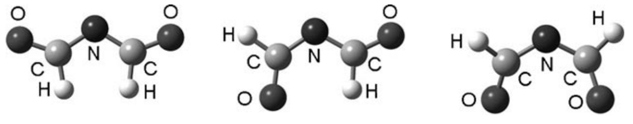


Figure 5. Computed isomers of the dfa anion.

X-ray Study of [K(18-crown-6)][N(CHO)₂]

To the best of our knowledge, no X-ray data of any diformylamide salts have been published yet. Since we did not succeed in obtaining single crystals of K^+dfa^-, the compound was recrystallized in the presence of 18-crown-6 ether in THF. [K(18-crown-6)][dfa] crystallizes in the orthorhombic space group $P2_12_12_1$ with four formula units per cell (Table 2). Each asymmetric unit consists of single independent K^+(18-crown-6) and dfa components with two strong cation···anion contacts (*d*(K−N) = 3.020(1), *d*(K−O) = 2.779(1) Å; Figure 7). However, there are no bridging interactions of the dfa anions, hence no coordination polymer was found.

In agreement with our computation (Table S2 in Supporting Information) the anion adopts a (*E*,*E*)-conformation with an almost planar C_{2v} symmetric dfa anion (dihedral angles: O1-C1-N1-C2 179.1° and C1-N1-C2-O2 179.0°, Figure 7). The O1−C1 and O2−C2 bond lengths amount to 1.227 and 1.193 Å, respectively, which is in the range expected for a C=O double bond (*cf.* d_{cov}(C=O) = 1.230 Å).[41] The bond lengths of 1.319 Å and 1.339 Å for the N1−C1 and

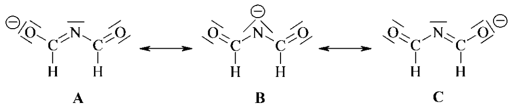


Figure 6. Lewis representations of the (*E*,*E*)-diformylamide anion.

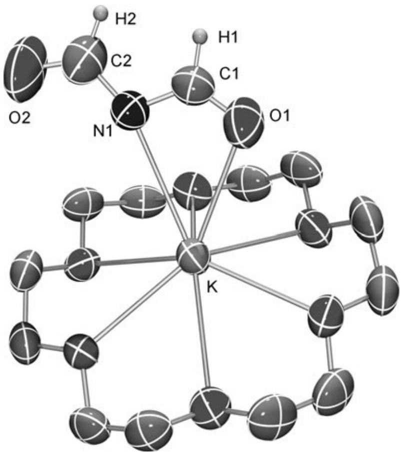


Figure 7. ORTEP drawing of the molecular structure of K(18-crown-6)$^+$ $[N(CHO)_2]^-$ in the crystal. Thermal ellipsoids with 50 % probability at 295 K. Hydrogen atoms of the crown ether are omitted for clarity. Selected bond lengths [Å] and angles [°]: O1−C1 1.227(4), N1−C1 1.319(4), K−O1 2.779(3), O2−C2 1.193(5), N1−C2 1.339(5), K−N1 3.020(3); C1-N1-C2 114.0(3), N1-C2-O2 126.8(5), K-O1-C1 99.3(2), N1-C1-O1 124.9(3), N1 K-O 145.60(8), K-N1-C1 86.2(2).

N1−C2 bonds lie in the range between a CN double and single bond (d_{cov}(C=N) = 1.270; d_{cov}(C−N) = 1.470 Å).[41] The N1-C1-O1 angle of 124.9° and 126.8° for the N1-C2-O2 angle correspond to formal sp^2 hybridized nitrogen. Compared to the free acid Hdfa, the C-N-C angle decreases from 122.5 to 114.0°, which can be explained on the basis of the VSEPR model,[44] requiring larger space for the lone pairs in the anion.

Synthesis, Properties, and Structure of Alkali and Silver Formylcyanoamides, M[N(CHO)CN]

In a modified literature synthesis,[9] formylcyanoamide salts were prepared in a two step procedure: First, the alkali methoxide was treated with cyanoamide to give the corresponding alkali cyanoamide salt in situ. Finally, addition of ethyl formate yields the alkali formylcyanoamide [Eq. (6) and (7)]. The hitherto unknown silver salt was obtained by salt metathesis reaction according to Equations (8) and (9).

$$NaOCH_3 + H_2NCN \rightarrow Na[HNCN] + HOCH_3 \tag{6}$$

$$Na[HNCN] + H_5C_2OCHO \rightarrow Na[N(CHO)CN] + HOC_2H_5 \tag{7}$$

$$\begin{aligned} &AgNO_3\ (aq) + Na[N(CHO)CN]\ (aq) \rightarrow \\ &Ag[N(CHO)CN] \downarrow + NaNO_3\ (aq) \end{aligned} \tag{8}$$

$$M[N(CHO)CN] + H_2O \rightarrow M[HCO_2] + H_2NCN \tag{9}$$

Alkali formylcyanoamide (fca) salts are moisture sensitive and decompose slowly to alkali formates in the presence of traces of water [Eq. (9)] as shown by ^{13}C NMR studies. The almost water-insoluble silver formylcyanoamide is very sensitive to light and heat. It decomposes within 3 h in daylight and even in the dark at ambient temperature after 24 h. Salts of formylcyanoamide are easily characterized by ^{1}H, ^{13}C, and ^{14}N NMR spectroscopy (^{1}H NMR: 8.49 ppm, *cf.* 8.00 ppm for (*Z*)-*N*-methylformamide (*Z*)-MeN(H)-C*H*O);[39] ^{13}C NMR: 172.9 and 123.4 ppm, *cf.* 165.4 ppm for (*E*)-*N*-methylformamide (*E*)-MeN(H)*C*HO)[39] and 128.7 ppm benzoylcyanoamide PhC(O)N(H)*C*N);[45] ^{14}N NMR: −190 and −245 ppm *cf.* −184 ppm for H_2NC*N*[46] and −268 ppm for HC(O)^{15}*N*H$_2$).[47] Experimentally observed IR and Raman data of several formylcyanoamide salts are listed in Table 4 together with computed vibrational data which have been used for an approximate assignment. DSC experiments revealed no melting point for the lithium salt since exothermic decomposition starts at 194 °C, while Na$^+$fca$^-$ melts at 253 °C and decomposes above 301 °C. Similar findings are obtained for K$^+$fca$^-$ (m.p. 182 °C, T_{dec} = 259 °C).

Computations showed two isomers (Figure 8) with the (*E*)-conformer slightly favored over the (*Z*)-conformer by 1 kcal mol^{-1}. Selected structural data of both isomers can be found in Table S3 in the Supporting Information. The electronic structure is best explained by resonance between the

Table 4. Computed and experimental vibrational data of fca salts (cm^{-1}) along with an approximate assignment.[a]

assignment	B3LYP/ 6-31G(d,p)[b]	Li$^+$fca$^-$ Raman[c]	IR[d]	Na$^+$fca$^-$ Raman[c]	IR[d]	K$^+$fca$^-$ Raman[c]	IR[d]	Ag$^+$fca$^-$ Raman[c]	IR[d]
ν_{C-H}	2762 (101,235)	2910 (2)	2896 w	2882 (3)	2882 w	2857 (3)	2857 m	2916 (2)	2894 w
$\nu_{C\equiv N}$	2252 (102,391	2210 (10)	2202 s	2180 (10)	2207 s	2178/2142 (9)	2196 s	2181 (10)	2184 s
$\nu_{C=O}$	1748 (4,782)	1594/1573 (2)	1589 vs	1578 (4)	1597 vs	1606/1592 (2)	1622 vs	1598 (2)	1614 s
δ_{C-H}	1442 (11,6)	1384 (3)	1388 m	1383 (3)	1384 m	1402 m	1402 m	1390 (2)	1396 w
$\nu_{as,C-N}$	1358 (10,157)	1328 (9)	1334 s	1329/1300 (4)	1320 s	1330/1306 (1)	1313 s	1319 (1)	1292 m
$\nu_{s,C-N}$	1094 (5,59)	1006 (2)	1090 w	984 (3)	1086 m	1001 (1)	1080 s	–	1084 w
γ_{C-H}	1039 (3,4)	864 (3)	1001 w	843 (3)	963 w	882 (1)	930 w	–	–
δ_{NCN}	638 (8,4)	617 (1)	640 w	613 (1)	638 w	642 (10)	642 m	634 (6)	–
δ_{NCO}	607 (4,3)	604 (1)	600 m	–	608 m	611 (1)	592 m	607 (1)	–
γ_{NCN}	578 (2,9)	543 (1)	540 m	522 (1)	524 m	–	553 w	556 (1)	–
$\delta_{NC\text{-}N\text{-}CHO,bending}$	200 (6,8)	262 (9)	–	216 (4)	–	230 (4)	–	236 (3)	–
$\gamma_{NC\text{-}N\text{-}CHO,twist}$	191 (1,18)	158 (4)	–	132 (5)	–	140 (3)	–	–	–

[a] Data correspond to the (*E*)-conformer of fca anion. [b] Unscaled calculated frequencies; in round brackets: IR intensities (km mol^{-1}), Raman activities (Å^4 amu^{-1}). [c] Experimental Raman intensity scaled to the maximum value 10. [d] KBr pellet. [e] ATR sensor.

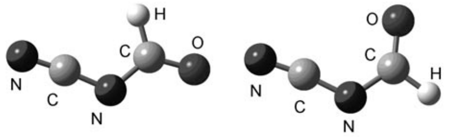


Figure 8. Computed conformers of the fca anion.

Lewis representations shown in Figure 9. While representation **A** describes a formylcarbodiimide, **B** corresponds to a formylcyanoamide, and **C** can be classified as an iminolate. According to NBO analysis[48–51] formylcyanoamide **B** seems to possess the largest weight.

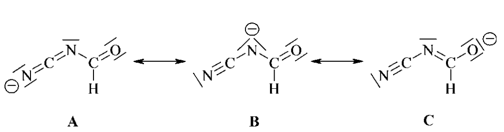


Figure 9. Lewis representations of the (*E*)-formylcyanoamide anion.

X-ray Study of [K(18-crown-6)][N(CHO)CN]

To the best of our knowledge, no X-ray data of any formylcyanoamide salts is available. In analogy to K^+dca^-, no single crystals of K^+fca^-could be obtained directly. Instead, K^+fca^- was recrystallized in the presence of 18-crown-6 ether in THF. [K(18-crown-6)][fca] crystallizes in the monoclinic space group *P*c with two formula units per cell (Table 2). The asymmetric unit consists of the ion pair K(18-crown-6)$^+$/[N(CHO)CN]$^-$ (Figure 10). Strong cation–anion interactions lead to chains of alternating K(18-crown-6)$^+$ and fca ions. Every fca ion forms a bridge between two cations, one interaction via the nitrogen atom of the cyano group and one via the oxygen atom of the formyl group (Figure 11).

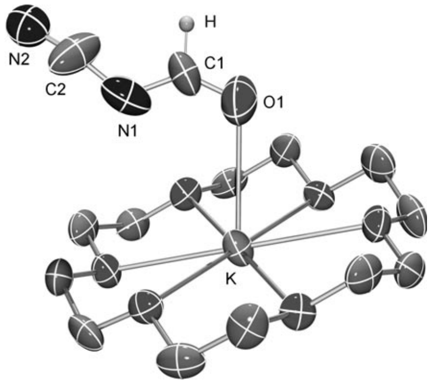


Figure 10. ORTEP drawing of the molecular structure of K(18-crown-6)$^+$ [N(CHO)CN]$^-$ in the crystal. Thermal ellipsoids with 30% probability at 295 K. Hydrogen atoms of the crown ether are omitted for clarity. Selected bond lengths [Å] and angles [°]: O1–C1 1.174(10), N1–C2 1.275(13), K1–O1, 2.811(7), N1–C1 1.213(11), N2–C2 1.151(13), K–N2 2.823(7); C1-N1-C2 123.0, N1-C2-N2 161.9(9), N1-C1-O1 136.0(9), K1-O1-C1 113.4(6).

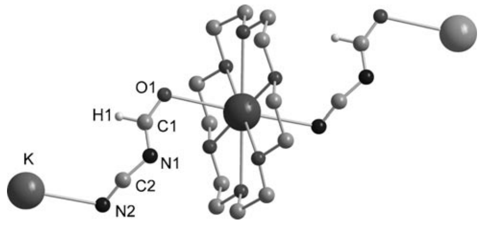
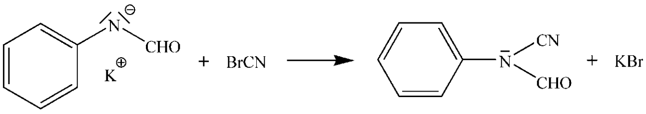


Figure 11. Cation–anion interactions in K(18-crown-6)$^+$[N(CHO)CN]$^-$ resulting in the formation of chains throughout the unit cell. Hydrogen atoms of the crown ether are omitted for clarity.

As predicted by theory, the anion was observed in the energetically favored (*E*)-conformation. In contrast to the planar C_s symmetric anion computed for the gas phase, the experimental data revealed a strong distortion from planarity as displayed by the N-C-N-C torsion angle of 108.2°. The N1-C2-N2 angle with 161.9° is also much smaller than calculated for the gas phase ion, where a value of 174.9° was estimated. These strong deviations may be attributed to the considerable cation···anion contacts. The observed O1–C1 bond length is 1.174 Å, which is in accordance with a C=O double bond. The N–C distances amount to 1.151 along the cyano group, and to 1.213 Å and 1.275 Å along the C-N-C moiety, respectively.

Synthesis, Properties, and Structure of Phenylformylcyanoamide

The first synthesis of phenylformylcyanoamide was achieved through the reaction of potassium phenylformylamide[52] with one equivalent of cyanogen bromide in acetonitrile (Scheme 1). Recrystallization from chloroform yields pure phenylformylcyanoamide.



Scheme 1. Synthesis of phenylformylcyanoamide.

Although phenylformylcyanoamide is neither hygroscopic nor air sensitive, it should be stored under inert gas since it slowly decomposes in the presence of moisture according to Equation (10). The labile phenylcyanoamide reacts further to give the trimer.[53]

$$PhN(CHO)CN + H_2O \rightarrow HCO_2H + Ph(H)NCN \qquad (10)$$

Pure phenylformylcyanoamide melts at 55°C and vaporizes at temperatures above 195°C at standard pressure. ^{1}H NMR spectroscopic studies revealed two resonances: A singlet at 9.02 ppm (*cf.* 8.55 ppm for *N,N*-diphenylformamide Ph_2NCHO)[54] and a multiplet in the typical aryl range

(7.50–7.18 ppm, *cf.* 7.58–6.99 ppm for *N*-phenylformamide).[54] The ^{13}C NMR spectrum shows a singlet resonance in the expected range of formamides (163.5 ppm, *cf.* 165.4 ppm for (*E*)-*N*-methylformamide (*E*)-MeN(H)-*C*HO),[39] four aryl resonances (130.7, 129.7, 129.4, and 127.3; *cf.* 140.9–124.0 *N,N*-diphenylformamide),[54] and a cyanoamide resonance (116.3 ppm, *cf.* 111.2 ppm for *N*-phenylcyanoamide PhN(H)*C*N).[55] Two singlets are found in the ^{14}N NMR spectrum at −159 ppm (*cf.* −164 ppm for 2,6-dichlorphenyl-$^{15}N(H)C^{15}N$)[56] and at −203 ppm (*cf.* −207 ppm for diformamide). Selected vibrational data are listed in Table S4 in the Supporting Information.

Two isomers of phenylformylcyanoamide were found at the B3LYP/6-31G(d,p) level of theory (Figure 12). Both isomers are separated by only 1 kcal mol^{-1} and can be regarded as conformers with respect to rotation about the N(CN)−CHO bond (Table S5 in the Supporting Information).

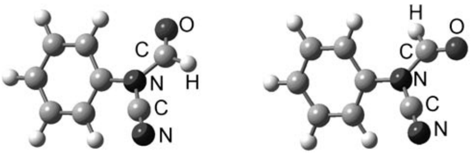


Figure 12. Computed isomers of phenylformylcyanoamide.

Some Aspects with Respect to Alkali Dicyanoamides, M[N(CN)$_2$], the Free Acid, HN(CN)$_2$, and Phenyldicyanoamide, Ph-N(CN)$_2$

Synthesis and properties of alkali dicyanoamides have been studied intensively over the last decades.[10–23] We want to focus here on covalently bound dicyanoamides, for which little is known. Alkali dicyanoamides are stable in neutral aqueous solution; however, they tend to polymerize at lower pH values. Hence, all attempts to isolate the free acid dicyanoamide, HN(CN)$_2$ have failed. One of the reasons for the instability of HN(CN)$_2$ is the formation of the carbodiimide isomer upon protonation, or more general, upon electrophilic attack of the dca anion. Carbodiimides are very prone to polymerization. According to NBO analysis, at least three Lewis representations including carbodiimide structures (**A** and **C**, Figure 13) are needed to properly explain the electronic structure of the dicyanoamide ion. Arising from a strong delocalization of the out of plane lone pair (almost pure p atomic orbital) at the central nitrogen atom into the two π* C−N bonds, a lot of the anion charge sits on the terminal nitrogen atoms, decreasing the basicity of the central nitrogen atom. The computed partial charges support this finding since both the central and the terminal nitrogen atoms possess almost the same value for the negative partial charges (NPA charges: $q(N_{terminal}) = -0.58/q(N_{central}) = -0.72$; *cf.* AIM charges: $q(N_{terminal}) = -1.39/q(N_{central}) = -1.34\,e$). Accordingly, the HOMO possesses large coefficients at the terminal nitrogen atoms (Figure 14).

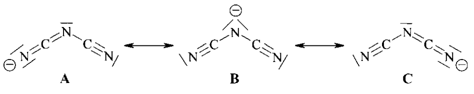


Figure 13. Lewis representations of the dca anion.

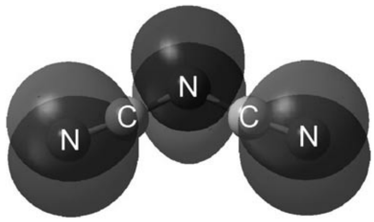


Figure 14. HOMO of the dca anion with B_1 symmetry.

A good hint for the prefered reaction of the terminal nitrogen atoms during an electrophilic attack can be observed experimentally when, for example, lithium dicyanoamide is crystallized in the presence of TMEDA (*N,N,N′,N′*-tetramethylethylendiamine, Figure 15). Chains of Li(TMEDA)$^+$ dca$^-$ units are found with the dca anion bridging two Li(TMEDA)$^+$ ions by means of the terminal nitrogen atoms. No contacts between the central amide nitrogen atom with the cations can be found. The Li$^+$ ion is bonded to each nitrogen atom of the TMEDA molecule and to one terminal nitrogen atom of both bridging dca anions, thus forming a tetrahedral coordination environment around the lithium cation with Li−N distances between 1.97–2.11 Å.

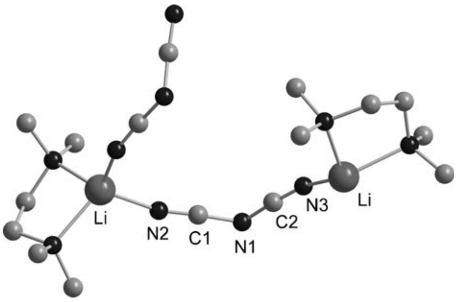
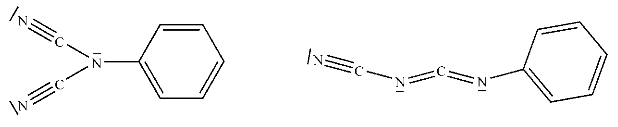


Figure 15. Part of the molecular structure of Li(TMEDA)$^+$dca$^-$ in the crystal. Hydrogen atoms of TMEDA are omitted for clarity. Selected bond lengths [Å] and angles [°]: N1−C2 1.3010(2), N1−C1 1.3075(1), N2−C1 1.1410(1), N2−Li 1.9876(2), N3−C2 1.1473(1), N3−Li 1.9722(2); C1-N1-C2 118.636(5), N1-C2-N3 173.691(9), N1-C1-N2 174.342(4), C2-N3-Li 155.011(7), C1-N2-Li 156.900(4).

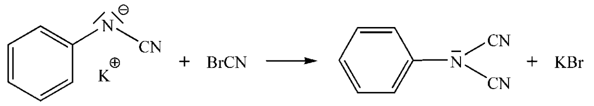
Phenyldicyanoamide

As described before, covalently bound dicyanoamides can formally be prepared by an alkyl or aryl electrophilic attack at either the central amide nitrogen atom or at the terminal nitrogen atoms of the dca anion. Hence, two structural isomers of R(N(CN)$_2$) can be formed as shown in Scheme 2. According to B3LYP/(6-31G(d,p) calculations, the carbodiimide isomer is favored over the dicyanoamide isomer by 10.0 kcal mol^{-1}.



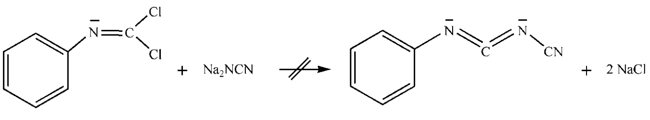
Scheme 2. Isomers of $PhN(CN)_2$: phenyldicyanoamide (left) and phenylcyanocarbodiimide (right).

The first report on monomeric aryldicyanoamides was published by Biechler in 1935 and the first alkyldicyanoamides by Benders and Hackmann in 1972.[57,58] While the synthesis of elementorganic dicyanoamides/cyanocarbodiimides was a research focus of the 1960s to late 1980s,[59,60,61] recent works mainly deal with the application of covalently bound dicyanoamides in electro- and polymer chemistry.[62] Köhler and Jäger were the first who addressed explicitly the carbodiimide/dicyanoamide problem as they studied phenyldicyanoamide and phenylcyanocarbodiimide.[63] We prepared phenyldicyanoamide in a slightly modified synthetic procedure from potassium phenylcyanoamide[53] and cyanogen bromide in acetonitrile (Scheme 3) and recrystallized from chloroform.



Scheme 3. Synthesis of phenyldicyanoamide.

According to Köhler and Jäger, phenylcyanocarbodiimide[63] can be obtained from the reaction of phenylisocyanide dichloride[64] with disodium cyanoamide[65] (Scheme 4), a reaction which we could not confirm.



Scheme 4. Failed synthesis of phenylcyanocarbodiimide according to Reference [63].

Similar to alkali dicyanoamides, phenyldicyanoamide is neither moisture nor air sensitive and is thermally stable up to 187 °C with a melting point of 92 °C (literature reference: 81 °C).[63] The ^{13}C NMR spectrum reveals beside the aryl peaks (133.4, 130.4, 127.5, and 116.1; *cf.* 139.6–114.4 *N*-phenylcyanoamide),[55] one resonance in the cyanoamide range (103.5 ppm, *cf.* 111.2 ppm for *N*-phenylcyanoamide PhN(H)*C*N).[55] On the other hand, two resonances are found in the ^{14}N NMR spectrum (−154 ppm, *cf.* −164 ppm 2,6-dichlorphenyl-^{15}N(H)C^{15}*N*)[56] and −323 ppm, *cf.* −322 ppm for 3,5-dichlorphenyl-^{15}*N*(H)C^{15}N).[56] Selected experimental vibrational data are listed in Table 5 along with the calculated data.

While structural data of organotin cyanocarbodiimides is available,[66] no X-ray structure analysis of a covalently bound dicyanoamide species has been published. Single crystals of phenyldicyanoamide suitable for X-ray structure analysis have been obtained from recrystallization in chloroform. Phenyldicyanoamide crystallizes in the monoclinic space group $P2_1/c$ with four units per cell (Table 2).

Table 5. Computed and experimental vibrational data of phenyldicyanoamide along with those of K^+dca^- (cm^{-1}).

assignment	B3LYP/ 6-31G(d,p)[a]	phenyldicyanoamide Raman[b]	 IR[c]	K^+dca^- Raman[b]	 IR[d]
$\nu_{s,C-H,Ph}$	3222(290,5)	3066(7)	3059 w	–	–
$\nu_{as,C-H,Ph}$	3203(108,8)	2984(3)	2961 w	–	–
$\nu_{s,C\equiv N}$	2374(129,74)	2262(10)	2264 m	2212(10)	2260 s
$\nu_{as,C\equiv N}$	2353(106,146)	2225(2)	2230 s	2176/ 2158(2)	2139 vs
$\nu_{s,C=C,Ph}$	1655(48,49)	1592(4)	1563 s	–	–
$\nu_{as,C=C,Ph}$	1537(2,79)	1462(1)	1490 vs	–	–
$\delta_{s,C-H,Ph}$	1374(0.3,1)	–	1347 s	–	–
$\nu_{as,C-N}$	1268(2,40)	–	1262 s	–	1322 s
$\nu_{C(Ph)-N}/\nu_{s,C-N}$	1260(39,117)	1240(6)	1237 vs	914(2)	915 s
$\delta_{as,C-H,Ph}$	1214(6,3)	1183(2)	1182 m	–	–
$\delta_{s,CCC,Ph}$	1066(6,4)	1035(1)	1025 w	–	–
$\delta_{as,CCC,Ph}$	1015(17,1)	1001(7)	1003 w	–	–
$\gamma_{as,C-H,Ph}$	918(2,4)	898(1)	902 w	-	-
$\gamma_{s,C-H,Ph}$	768(0.3,53)	752(1)	748 s	–	–
$\delta_{s,NCN}$	640(3,5)	633(2)	638 m	666(2)	666 m
$\delta_{as,NCN}$	532(1,0.2)	526(1)	–	–	525 s

[a] Unscaled calculated frequencies; in round brackets: IR intensities (km mol^{-1}), Raman activities ($Å^4$ amu^{-1}). [b] Experimental Raman intensity scaled to the maximum value 10. [c] ATR sensor. [d] KBr pellet.

Figure 16 shows the molecular structure of phenyldicyanoamide, revealing a non-planar species (dihedral angle N1-C1-N3-C2 = 168.9°). A slight torsion of the phenyl ring (19.7°) with respect to the NCN plane is also observed. The N1−C1 and N2−C2 bond lengths are 1.136 Å and 1.145 Å, respectively, consistent with the presence of a triple bond

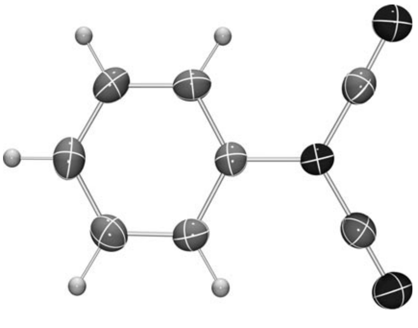
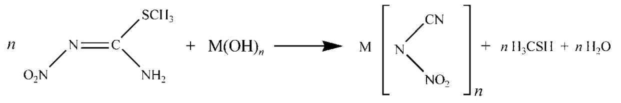


Figure 16. ORTEP drawing of the molecular structure of phenyldicyanoamide. Thermal ellipsoids with 50 % probability at 295 K. Selected bond lengths [Å] and angles [°]: N1−C1 1.136(3), N3−C1 1.360(3), N3−C3 1.452(3), N2−C2 1.145(3), N3−C2 1.352(3); N1-C1-N3 178.2(3), N3-C3-C4 119.1(2), C1-N3-C3 121.1(2), N2-C2-N3 179.4(2), C1-N3-C2 117.0(2), C2-N3-C3 121.4(2).

(d_{cov}(C≡N) = 1.150 Å).[41] The C1/2–N3 distances lie between 1.352 Å and 1.360 Å, indicating a bond order between 1 and 2 (d_{cov}(C=N) = 1.270 Å and d_{cov}(C–N) = 1.470 Å).[41]

Synthesis, Properties, and Structure of Alkali Nitrocyanoamides, M[N(NO$_2$)CN]

Alkali nitrocyanoamides (nca) can be prepared by the reaction of the base MOH with *S*-methyl-*N*-nitroisothiourea[26] (Scheme 5).[27a,b]



Scheme 5. Synthesis of nitrocyanoamide salts (M = Li, Na, Cs (*n* = 1) and Ba (*n* = 2)).

Crystals of Li$^+$nca$^-$ and Li$^+$nca$^-$·2 H$_2$O are very moisture sensitive and deliquesce within seconds while all other examined alkali nca salts can be handled without inert gas atmosphere. Unlike the dca and fca salts, all investigated nca compounds are heat and shock-sensitive. However, they are thermally stable up to over 215 °C and decompose in exothermic reactions upon further heating.[24,28] Results of the DTA/TGA experiments are listed in Table 6.

Table 6. Thermal properties of alkali nitrocyanoamides and barium nitrocyanoamide.

M[N(NO$_2$)CN]$_n$	m.p. [°C]	T_{dec} [°C][a]	loss of mass [%]
Li[N(NO$_2$)CN]	–[b]	215	54
Na[N(NO$_2$)CN]	203	254	38
Cs[N(NO$_2$)CN]	93	312	19
Ba[N(NO$_2$)CN]$_2$	–[b]	293	50

[a] T_{dec} = decomposition temperature (onset); [b] no m.p. was observed.

The nca anion is easily detected by means of Raman, IR, and NMR spectroscopy (^{14}N, ^{13}C), as well as FAB$^-$. Vibrational data and assignments are listed in Table 7. Three resonances are observed in the ^{14}N NMR spectrum of nca salt solutions which are in the typical range of nitramides (−2 ppm, *cf.* −9 ppm for [N(*N*O$_2$)$_2$]$^-$),[67] nitramines (−165 ppm, *cf.* −143 ppm 2-pyridyl-*N*(H)NO$_2$),[68] and cyanoamides (−178 ppm, *cf.* −184 ppm for H$_2$NC*N*), respectively.[46] A single resonance is found for the cyano group in the ^{13}C NMR experiment (116.7 ppm, *cf.* 111.2 ppm for PhN(H)*C*N, *N*-phenylcyanoamide).[55]

The electronic structure is best described by a series of different resonance structures such as nitrocarbodiimide representations (**A** and **B** in Figure 17), nitrocyanoamide structures **C** and **D**, or *N*-cyanodiazen-*N′*,*N′*-dihydroxylate **E**. According to NBO analyses, Lewis representations **C** and **D** are the best descriptions of the electronic structure.

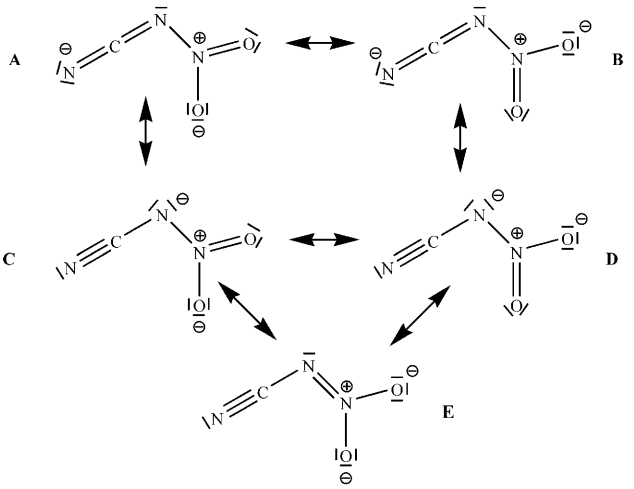


Figure 17. Lewis representations of the nca anion.

Besides powder data,[27a] no single crystal data of the sodium nitrocyanoamide salt are available so far. Na$^+$nca$^-$ crystallizes in the monoclinic space group *P*2$_1$/*n* with four formula units per cell (Table 2). The molecular structure is shown in Figure 18.

Table 7. Computed and experimental vibrational data of nca salts (cm^{-1}) along with an approximate assignment.

assignment	B3LYP/ 6-31G(d,p)[a]	Li$^+$nca$^-$ Raman[b]	IR[c]	Na$^+$nca$^-$ Raman[b]	IR[c]	Cs$^+$nca$^-$ Raman[b]	IR[c]	Ba^{2+}(nca$^-$)$_2$ Raman[b]	IR[c]
$\nu_{C\equiv N}$	2266 (132,241)	2229 (10)	2211 s	2192 (10)	2196 s	2184 (10)	2178 vs	2219 (1)	2212 s
$\nu_{N=O}$	1549 (2,386)	1540 (2)	1438 s	1466 (1)	1450 s	1441 (1)	1430 s	1529 (0.5)	1418 s
$\nu_{N–N}$	1357 (4,626)	1290 (1)	1276 vs	1319 (2)	1287 vs	1257 (1)	1260 s	1299 (1)	1276 vs
$\nu_{C–N}$	1199 (13,22)	1173 (5)	1173 m	1181 (3)	1178/1168 m	1166 (3)	1160 s	1178 (8)	1172 m
δ_{CNN}	965 (14,17)	982 (5)	972 w	967 (6)	984/967 w	958 (2)	960 m	982 (10)	979 m
γ_{ONO}	781 (8,1)	–	774 w	–	776 w	–	772 m	–	764 m
δ_{ONO}	770 (8,1)	778 (3)	760 w	774 (5)	764 m	766 (5)	764 m	966 (6)	–
δ_{NNO}	590 (6,0)	622 (1)	–	610 (2)	–	599 (1)	–	623 (3)	–
γ_{NCN}	560 (2,13)	537 (1)	536 m	547 (1)	545 m	–	548 m	532 (1)	528 m
γ_{NCN}	515 (2,13)	506 (1)	520 m	515 (2)	511 m	509 (1)	512 m	498 (2)	509 m
$\delta_{NC\text{-}N\text{-}NO2,bending}$	200 (4,3)	227 (4)	–	230 (2)	–	226 (3)	–	221 (5)	–
$\gamma_{NC\text{-}N\text{-}NO2,twist}$	144 (0,3)	151 (5)	–	135 (3)	–	–	–	143 (2)	–

[a] Unscaled calculated frequencies; in round brackets: IR intensities (km mol^{-1}), Raman activities (Å^4 amu^{-1}). [b] Experimental Raman intensity scaled to the maximum value 10. [c] ATR sensor.

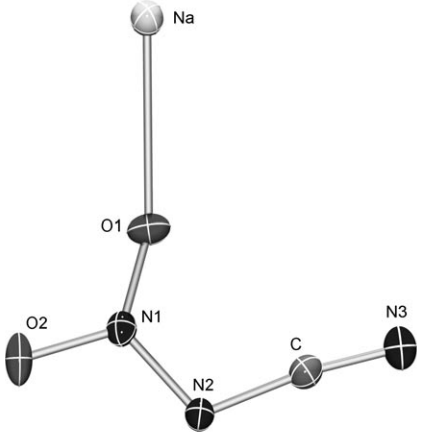


Figure 18. ORTEP drawing of the molecular structure of Na^+nca^-. Thermal ellipsoids with 50% probability at 295 K. Selected bond lengths [Å] and angles [°]: N1–O1 1.234(1), N1–N2 1.338(1), C–N3 1.148(2), N1–O2 1.250(1), N2–C 1.340(2), Na–O1 2.369(1); N1-N2-C 111.2(1), Na-O1-N1 143.5(1), O1-N1-N2 122.1, N2-C-N3 172.4(1), O1-N1-O2 122.1(1), O2-N1-N2 115.8(1).

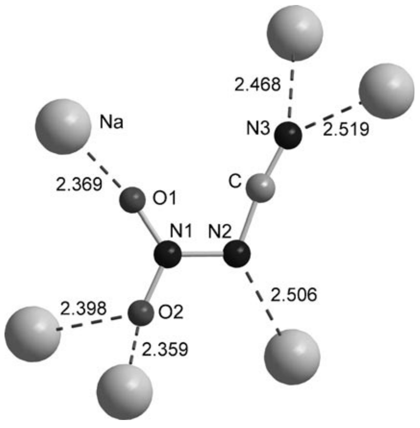


Figure 19. Cation–anion interactions in Na^+nca^-. Distances in Å.

A great diversity of bonding modes is found for the nca anion which is surrounded by six sodium cations. The CN group coordinates two neighboring Na^+ centers, the NO_2 moiety coordinates three cations through the oxygen atoms in both mono and bidentate fashion, while the amide nitrogen atom also coordinates an additional Na^+ (Figure 19). The Na^+ ion is surrounded by three O and three N donor atoms, leading to a coordination number of six. These strong cation–anion interactions lead to an interesting three-dimensional network arrangement of the ions in the solid with chains of Na^+ and nca^- stacked one upon the other.[1]

Partial double bond character can be assumed for the N–CN and N–NO_2 bonds with distances of 1.340(1) Å and 1.338(1) Å, respectively, while the C–N3 bond length of 1.148(1) Å corresponds to a triple bond. The resonance stabilized nca anion is almost planar with an O1-N1-N2-C dihedral angle of 3.3°.

Ionic Liquids

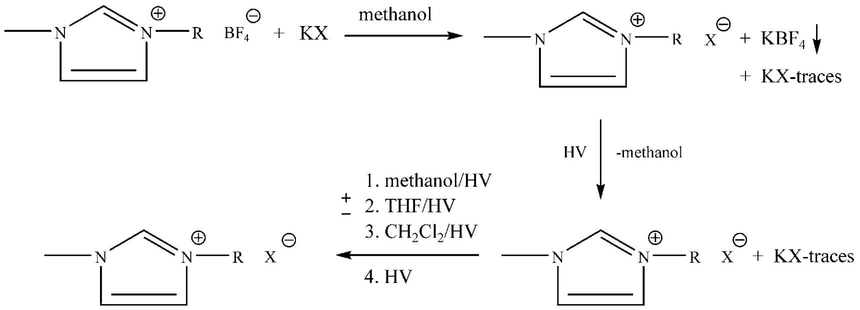
Ionic liquids (ILs) of resonance stabilized amides are readily prepared from the reaction of the amide based pseudohalide potassium salts with imidazolium tetrafluoroborate salts (e.g., $BMIM^+BF_4^-$, Scheme 6).[69] While the potassium and imidazolium salts are soluble in methanol, potassium tetrafluoroborate precipitates and can be separated by filtration. A specific drying procedure involving stepwise addition and removal of dried methanol, THF, and dichloromethane, followed by the removal of traces of water or solvent molecules under high vacuum (HV), is necessary to obtain pure ionic liquids of the type, for example, $BMIM^+X^-$. Tables 8 and 9 summarize the spectroscopic data of all ionic liquids of resonance stabilized amides we discuss here.

In contrast to the high energy-density alkali and silver nca salts,[24,28] the ionic liquids with nitrocyanoamide anion and a bulky organic cation are neither heat nor shock sensitive,

Table 8. Thermal properties of amide based ionic liquids [$RMIM^+X^-$] (R = alkyl: E = ethyl, B = n-butyl, H = n-hexyl; MIM = methylimidazolium; X = resonance stabilized amide).

amide	R	M [g mol^{-1}]	T_m/T_g [°C][a]	T_{dec} [°C][b]
dca[72]	ethyl[72]	177.21	−12[72]	240[72]
dfa	ethyl	183.21	−18	213
fca	ethyl	180.21	−5	218
nca	ethyl	197.20	27	225
dca[73]	*n*-butyl[73]	205.26	−29[73]	240[73]
dfa	*n*-butyl	211.26	−26	221
fca	*n*-butyl	208.26	32	227
nca	*n*-butyl	225.25	−6	234
dca	*n*-hexyl	233.32	−48	246
dfa	*n*-hexyl	239.32	−41	228
fca	*n*-hexyl	236.32	−15	231
nca	*n*-hexyl	253.31	−38	239

[a] T_m = m.p., T_g = temperature of phase transition. [b] T_{dec} = decomposition temperature (onset).



Scheme 6. Synthesis and post-synthetical treatment procedure of ionic liquids of resonance stabilized amides (R = ethyl, n-butyl, n-hexyl; X = amide based pseudohalide; HV = high vacuum; ± = addition of dried solvent and removal in HV).

Table 9. Spectroscopic data of amide based ionic liquids [RMIM$^+$X$^-$] (R = alkyl: E = ethyl, B = *n*-butyl, H = *n*-hexyl; MIM = methylimidazolium; X = resonance stablized amide).

amide	R	Raman[a] [cm^{-1}]	IR[a] [cm^{-1}]	δ(^{13}C)[b] [ppm]	δ(^{14}N)[b] [ppm]	δ(^{1}H)[b] [ppm]
dfa	ethyl	ν_{CH} 2860, ν_{CO} 1682, 1575	ν_{CH} 2863, ν_{CO} 1696, 1554	N-*C*HO, 181.3	*N*-CHO, −128	N-C*H*O, 8.95
dfa	*n*-butyl	ν_{CH} 2875, ν_{CO} 1687, 1569	ν_{CH} 2876, ν_{CO} 1696, 1561	N-*C*HO, 181.3	*N*-CHO, −128	N-C*H*O, 8.95
dfa	*n*-hexyl	ν_{CH} 2858, ν_{CO} 1683, 1566	ν_{CH} 2860, ν_{CO} 1697, 1558	N-*C*HO, 181.3	*N*-CHO, −128	N-C*H*O, 8.95
fca	ethyl	ν_{CH} 2859, ν_{CN} 2142, ν_{CO} 1570	ν_{CH} 2861, ν_{CN} 2148, ν_{CO} 1565	N-*C*HO, 172.9 *N*-*C*N, 123.4	N-C*N*, −190 *N*-CHO, −245	N-C*H*O, 8.49
fca	*n*-butyl	ν_{CH} 2867, ν_{CN} 2145, ν_{CO} 1566	ν_{CH} 2873, ν_{CN} 2150, ν_{CO} 1571	N-*C*HO, 172.9 *N*-*C*N, 123.4	N-C*N*, −190 *N*-CHO, −245	N-C*H*O, 8.49
fca	*n*-hexyl	ν_{CH} 2862, ν_{CN} 2156, ν_{CO} 1576	ν_{CH} 2859, ν_{CN} 2147, ν_{CO} 1584	N-*C*HO, 172.9 *N*-*C*N, 123.4	N-C*N*, −190 *N*-CHO, −245	N-C*H*O, 8.49
nca	ethyl	ν_{CN} 2171, ν_{NO} 1570, 1426, ν_{NN} 1259	ν_{CN} 2168, ν_{NO} 1572, 1424, ν_{NN} 1258	N-*C*N, 116.7	N-*N*O$_2$, −2 *N*-NO$_2$, −165 *N*-C*N*, −178	-
nca	*n*-butyl	ν_{CN} 2172, ν_{NO} 1566, 1418, ν_{NN} 1265	ν_{CN} 2169, ν_{NO} 1572, 1425, ν_{NN} 1260	N-*C*N, 116.7	N-*N*O$_2$, −2 *N*-NO$_2$, −165 *N*-C*N*, −178	-
nca	*n*-hexyl	ν_{CN} 2171, ν_{NO} 1569, 1417, ν_{NN} 1261	ν_{CN} 2168, ν_{NO} 1571, 1424, ν_{NN} 1259	N-*C*N, 116.7	N-*N*O$_2$, −2 *N*-NO$_2$, −165 *N*-C*N*, −178	-
dca	*n*-hexyl	ν_{CN} 2192, 2135	ν_{CN} 2228, 2125	N-*C*N, 118.9	N-C*N*, −229 *N*-CN, −368	-

[a] Only characteristic vibrations of the anion are listed. [b] Only characteristic shifts of the anion are listed.

and can therefore be prepared and stored in large scale. Nevertheless, this type of amide based ionic liquids can also be considered as "energetic ionic liquids" since the thermodynamically unstable amide anion is only kinetically stabilized by a bulky organic cation such as EMIM$^+$ or BMIM$^+$.[70] Amide based ionic liquids are very hygroscopic and immediately absorb water when exposed to air. The decomposition temperature of amide based ionic liquids ranges, depending on the counterion, between T_{dec} = 213 °C [EMIM$^+$ dfa$^-$] and 246 °C [HMIM$^+$dca$^-$] (Table 8). As shown in Table 8 ionic liquids of CHO- and NO$_2$-substituted amides are less stable compared to ILs with the dca anion. Moreover, the thermal stability increases along the series EMIM$^+$ X$^-$ < BMIM$^+$X$^-$ < HMIM$^+$X$^-$. Slow decomposition arising from hydrolysis of the formyl-based ILs is observed when exposed to air [Equations (11) and (12)].

$$[N(CHO)_2]^- + H_2O \rightarrow [HCO_2]^- + H_2NCHO \quad (11)$$

$$[N(CHO)CN]^- + H_2O \rightarrow [HCO_2]^- + H_2NCN \quad (12)$$

The initially colorless dfa-based ILs slowly turn red–brown, depending on the storage temperature. Hence, these ILs should be stored under nitrogen at temperatures below −5 °C. All other ILs can be stored at ambient temperature under nitrogen without any noticeable decomposition.

The experimentally determined melting points vary between −48 °C [HMIM$^+$dca$^-$] and 32 °C [BMIM$^+$fca$^-$] (Table 8), with the HMIM salts always possessing the lower melting point. It can be assumed that both the number and the strength of interionic interactions (coulomb and hydrogen bonding) as well as the size of the ions is responsible for the fairly wide range of observed melting points. So far we have not been able to crystallize any of the discussed ionic liquids without solvent. Solidification resulted only in glass formation, a well-known phenomenon of ionic liquids.[71]

Summary

The synthesis, structure, and bonding of alkali salts of resonance stabilized amides such as dfa, fca, nca, and dca are discussed on the basis of experimental and theoretical data. X-ray data of K(18-crown-6)$^+$dfa$^-$, K(18-crown-6)$^+$fca$^-$, Na$^+$nca$^-$, and Li(TMEDA)$^+$dca$^-$ reveal almost planar anions with strong cation–anion interactions resulting in network-like structures in the solid state. For comparison, the X-ray structures of covalently bound diformamide and phenyldicyanoamide have also been discussed.

Moreover, novel ionic liquids based on resonance stabilized amides have been prepared and fully characterized. Their synthesis starts with the potassium salts of the amides and the imidazolium tetrafluoroborate salts. All new compounds represent room temperature ionic liquids, except for BMIM$^+$fca$^-$ melting at 32 °C. These ionic liquids are neither heat nor shock sensitive, they are thermally stable up to over 200 °C, and can be prepared in large quantities.

Experimental Section

General Information

NMR: ^{1}H, ^{13}C{^{1}H}, and ^{14}N{^{1}H} NMR spectra were obtained on a JEOL EX 400 NMR spectrometer or on a JEOL EX 270 NMR spectrometer and were referenced either to protic impurities in the deuterated solvent (^{1}H) or externally to $SiMe_4$ (^{13}C{^{1}H}) or nitromethane (^{14}N{^{1}H}). IR: Perkin–Elmer Spectrum One FT-IR spectrometer with a DuraSampl*IR*II Diamond ATR sensor from SensIR Technologies or Nicolet 520 FT-IR spectrometer (KBr pellets). Raman: Perkin–Elmer Spectrum 2000 NIR FT equipped with a Nd:YAG laser (1064 nm). CHN analyses: Analysator Elementar Vario EL. MS: Jeol MStation JMS 700. DSC experiments: Perkin–Elmer Pyris 6 DSC or Setraram DSC 141. DTA/TGA experiments: Setraram TG-DTA 92.

X-ray Structure Determination

X-ray quality crystals of all considered species were selected in silicon oil at RT. All samples were mounted on a glass fiber and cooled to 200(2) K during measurement. Data for compounds Hdfa and Pfdca were collected on a NONIUS KappaCCD diffractometer, data for compounds Na^+ nca^- and Li(edta)dca were collected on a STOE IPDS diffractometer, and K(18-crown-6)$^+$dfa$^-$ and K(18-crown-6)$^+$fca$^-$ on a NONIUS CAD4 using Mo Kα radiation ($\lambda = 0.71073$). Crystallographic data are summarized in Table 2. Selected bond lengths and angles are available in Figure 2, 7, 10, 16, and 18. The structures were solved by direct methods (SHELXS-97 (Li(Edta)dca, K(18-crown-6)$^+$fca$^-$, K(18-crown-6)$^+$dfa$^-$), SIR-97 (Phdca, Nanca, and Hdfa)[72,73] and refined by full-matrix least squares procedures (SHELXL-97).[74] All non hydrogen atoms were refined anisotropically. In Li(Etda)dca the hydrogen atoms were included in the refinement at calculated positions using a riding model, in Hdfa and Phdca the hydrogen atoms were refined freely.

Synthetic Procedures

Hdfa: HCl (4.70 L; 0.21 mol) gas was added to a stirred suspension of sodium diformylamide (13.28 g; 0.14 mol) in dried diethyl ether (400 mL) at 0 °C. This mixture was allowed to warm up to ambient temperature and stirred for 3 h before filtration. The residue was washed with diethyl ether (200 mL), and the combined ether phases were concentrated. Addition of *n*-hexane (60 mL) yielded colorless crystals. Yield: 6.95 g (68 %); m.p.: 44 °C; b.p.: 198 °C; IR (KBr, 25 °C): $\tilde{\nu} = 3262$ (s), 2917 (m), 2898 (sh), 1745 (s), 1686 (vs), 1480 (m), 1412 (w), 1373/1347 (m), 1264 (m), 1188 (s), 1088/1041 (w), 796 (m), 649 (s), 527 cm^{-1} (m); Raman (200 mW, 25 °C): $\tilde{\nu} = 3256$ (1), 2955 (2), 2934 (1), 1739/1719 (10), 1450 (1), 1431 (5), 1372/1359 (0.4), 1264 (1), 1192/1167 (0.4), 1090/1077 (0.5), 1038 (0.3), 769 (0.3), 547 (9), 231 (1), 142 cm^{-1} (5); ^{1}H NMR ([D$_6$]DMSO, 400 MHz, 25 °C): $\delta = 11.16$ (s, 1H, NH), 8.83 ppm (s, 2H, CHO); ^{13}C NMR ([D$_6$]DMSO, 101 MHz, 25 °C): $\delta = 167.2$ ppm (s, CHO); ^{14}N NMR ([D$_6$]DMSO, 28.9 MHz, 25 °C): $\delta = -207$ ppm (s, $\Delta\nu^{1/2} = 507$ Hz, N-CHO); MS (EI$^+$, 70 eV, >5 %), *m/z* (%): 73 (95) [M], 45 (100) [M−CO], 44 (44) [M−CHO], 43 (15) [M−H−CHO], 29 (51) [CHO], 28 (23) [CO]; elemental analysis: calcd (%) for $C_2H_3NO_2$ (73.05): C 32.88, H 4.14, N 19.17; found: C 32.59, H 4.31, N 18.98.

Na$^+$dfa$^-$: Sodium methoxide (0.72 g; 13.3 mmol) was added to a stirred solution of diformamide (1.00 g 13.7 mmol) in dried THF (25 mL) at 0 °C. After stirring for 6 h, the reaction mixture was filtered, the residue washed with THF and subsequently dried in vacuum. Yield: 1.23 g (97 %); m.p.: 242 °C, $T_{\text{dec,onset}} = 286$ °C; IR (KBr, 25 °C): $\tilde{\nu} = 2833$ (m), 2716 (w), 1694 (s), 1591 (vs), 1388 (m), 1363 (s), 1291 (m), 1264 (m), 1089 (w), 778 (m), 605 cm^{-1} (m); Raman (200 mW, 25 °C): $\tilde{\nu} = 2862$ (2), 2776 (2), 1677 (10), 1422 (3), 1405 (1), 1274 (1), 1261 (2), 1063 (1), 602 (8), 320 cm^{-1} (2); ^{1}H NMR ([D$_6$]DMSO, 400 MHz, 25 °C): $\delta = 8.95$ ppm (s, CHO); ^{13}C NMR ([D$_6$]DMSO, 101 MHz, 25 °C): $\delta = 181.3$ ppm (s, CHO); ^{14}N NMR ([D$_6$]DMSO, 28.9 MHz, 25 °C): $\delta = -128$ ppm (s, $\Delta\nu^{1/2} = 1301$ Hz, N-CHO); MS (FAB$^-$, Xenon, 6 keV, *m*-NBA-matrix), *m/z* (%): 72 (3) [M], 73 (2) [M+H]; elemental analysis: calcd (%) for $C_2H_2NNaO_2$ (95.03): C 25.28, H 2.12, N 14.74; found: C 24.85, H 2.21, N 14.25.

Li$^+$dfa$^-$: Lithium *tert*-butoxide (1.60 g; 20.0 mmol) was added to a stirred solution of diformamide (1.50 g; 20.5 mmol) in dried THF (25 mL) at 0 °C. After stirring for 6 h, the reaction mixture was filtered, the residue washed with THF, and subsequently dried in vacuum. Yield: 1.48 g (94 %); $T_{\text{dec,onset}} = 175$ °C; IR (KBr, 25 °C): $\tilde{\nu} = 2856$ (w), 2747 (vw), 1694 (vs), 1604 (vs), 1386 (s), 1370 (s), 1287 (m), 1263 (m), 1055 (w), 785 (m), 618 cm^{-1} (m); Raman (200 mW, 25 °C): $\tilde{\nu} = 2847$ (1), 2766 (2), 1747/1709 (10), 1415 (2), 1313/1308 (1), 1268 (1), 1048 (1), 616 (4), 339 cm^{-1} (1); ^{1}H NMR ([D$_6$]DMSO, 400 MHz, 25 °C): $\delta = 8.95$ ppm (s, CHO); ^{13}C NMR ([D$_6$]DMSO, 101 MHz, 25 °C): $\delta = 181.3$ ppm (s, CHO); ^{14}N NMR ([D$_6$]DMSO, 28.9 MHz, 25 °C): $\delta = -128$ ppm (s, $\Delta\nu^{1/2} =$ 1301 Hz, N-CHO); MS (FAB$^-$, Xenon, 6 keV, *m*-NBA-matrix), *m/z* (%): 72 (5) [M], 73 (3) [M+H]; elemental analysis: calcd (%) for $C_2H_2LiNO_2$ (78.98): C 30.41, H 2.55, N 17.73; found: C 31.35, H 3.22, N 16.58.

K$^+$dfa$^-$: Potassium methoxide (1.10 g 15.7 mmol) was added to a stirred solution of diformamide (1.20 g; 16.4 mmol) in dried THF (25 mL) at 0 °C. After stirring for 6 h, the reaction mixture was filtered, the residue washed with THF, and subsequently dried in vacuum. Yield: 1.62 g (93 %); m.p.: 237 °C, $T_{\text{dec,onset}} = 384$ °C; IR (KBr, 25 °C): $\tilde{\nu} = 2838$ (w), 2771 (w), 1698 (s), 1560 (vs), 1387 (m), 1349 (m), 1282 (s), 1251 (m), 1130 (w), 740 (m), 610 cm^{-1} (m); Raman (200 mW, 25 °C): $\tilde{\nu} = 2853$ (1), 2771 (2), 1668 (10), 1421 (3), 1409 (1), 1294 (1), 1258 (2), 1051 (1), 593 (8), 317 cm^{-1} (2); ^{1}H NMR ([D$_6$]DMSO, 400 MHz, 25 °C): $\delta = 8.95$ ppm (s, CHO); ^{13}C NMR ([D$_6$]DMSO, 101 MHz, 25 °C): $\delta = 181.3$ ppm (s, CHO); ^{14}N NMR ([D6]DMSO, 28.9 MHz, 25 °C): $\delta = -128$ ppm (s, $\Delta\nu^{1/2} =$ 1301 Hz, N-CHO); MS (FAB$^-$, Xenon, 6 keV, *m*-NBA-matrix), *m/z* (%): 72 (2) [M], 73 (2) [M+H]; elemental analysis: calcd (%) for $C_2H_2KNO_2$ (111.14): C 21.61, H 1.81, N 12.60; found: C 21.22, H 1.70, N 12.09.

Na$^+$fca$^-$: A solution of cyanoamide (1.00 g; 23.8 mmol) in dried methanol (10 mL) was added slowly to a stirred solution of sodium methoxide (1.29 g; 23.8 mmol) in dried methanol (40 mL) at 0 °C. After stirring for 30 min, the reaction mixture was heated to boiling and ethyl formate (5.80 mL; 5.34 g, 72.0 mmol) was added. After 3 h reflux, all volatiles were removed in vacuum and the residue was dried in vacuum. Yield: 2.15 g (98 %); m.p.: 253 °C; $T_{\text{dec,onset}} = 301$ °C; IR (KBr, 25 °C): $\tilde{\nu} = 2882$ (w), 2207 (s), 1597 (vs), 1384 (m), 1320 (s), 1086 (m), 963 (w), 638 (w), 608 (m), 524 cm^{-1} (m); Raman (200 mW, 25 °C): $\tilde{\nu} = 2882$ (3), 2180 (10), 1578 (4), 1383 (3), 1329/1300 (4), 984 (3), 843 (3), 613 (1), 522 (1), 216 (4), 132 cm^{-1} (5); ^{1}H NMR ([D$_6$]DMSO, 400 MHz, 25 °C): $\delta = 8.49$ ppm (s, CHO); ^{13}C NMR ([D$_6$]DMSO, 101 MHz, 25 °C): $\delta = 172.9$ (s, CHO), 123.4 ppm (s, CN); ^{14}N NMR ([D$_6$]DMSO, 28.9 MHz, 25 °C): $\delta = -190$ (s, $\Delta\nu^{1/2} = 1156$ Hz, CN), −245 ppm (s, $\Delta\nu^{1/2} = 1927$ Hz, N-CHO); MS (FAB$^-$, Xenon, 6 keV, *m*-NBA-matrix), *m/z* (%): 69 (27) [M]; elemental analysis: calcd (%) for C_2HN_2NaO (92.03): C 26.10, H 1.10, N 30.44; found: C 25.86, H 1.21, N 29.91.

Li$^+$fca$^-$: A solution of cyanoamide (1.00 g; 23.8 mmol) in 10 mL dried methanol was added slowly to a stirred solution of lithium *tert*-butoxide (1.90 g; 23.8 mmol) in dried methanol (40 mL) at 0 °C. After stirring for 30 min, the reaction mixture was heated to boiling and ethyl formate (5.80 mL; 5.34 g, 72.0 mmol) was added. After 3 h reflux, all volatiles were removed in vacuum and the residue was dried in vacuum. Yield: 1.72 g (95 %); $T_{\text{dec,onset}} = 194$ °C; IR (KBr, 25 °C): $\tilde{\nu} = 2896$ (w), 2202 (s), 1589 (vs), 1388 (m), 1334 (s), 1090 (w), 1001 (w), 640 (w), 600 (m), 540 cm^{-1} (m); Raman (200 mW, 25 °C): $\tilde{\nu} = 2910$ (2), 2210 (10), 1594/1573 (2), 1384 (3), 1328 (9), 1006 (2), 864 (3), 617 (1), 604 (1), 543 (1), 262 (9), 158 cm^{-1} (4); ^{1}H NMR ([D$_6$]DMSO, 400 MHz, 25 °C): $\delta = 8.49$ ppm (s, CHO); ^{13}C NMR ([D$_6$]DMSO, 101 MHz, 25 °C): $\delta = 172.9$ (s, CHO), 123.4 ppm (s, CN); ^{14}N NMR ([D$_6$]DMSO, 28.9 MHz, 25 °C): $\delta = -190$ (s, $\Delta\nu^{1/2} = 1156$ Hz, CN), −245 ppm (s, $\Delta\nu^{1/2} = 1927$ Hz, N-CHO); MS (FAB$^-$, Xenon, 6 keV, *m*-NBA-matrix), *m/z* (%): 69 (21) [M]; elemental analysis: calcd (%) for C_2HLiN_2O (75.98): C 31.62, H 1.33, N 36.87; found: C 32.46, H 1.87, N 35.94.

K$^+$fca$^-$: A solution of cyanoamide (1.00 g; 23.8 mmol) in dried methanol (10 mL) was added slowly to a stirred solution of potassium methoxide (1.67 g; 23.8 mmol) in dried methanol (40 mL) at 0 °C. After stirring for 30 min, the reaction mixture was heated to boiling and ethyl formate (5.80 mL; 5.34 g, 72.0 mmol) was added. After 3 h reflux, all volatiles were removed in vacuum and the residue was dried in vacuum. Yield:

2.49 g (97 %); m.p.: 182 °C; $T_{\text{dec,onset}} = 259$ °C; IR (KBr, 25 °C): $\tilde{\nu} = 2857$ (m), 2196 (s), 1622 (vs), 1402 (m), 1313 (s), 1080 (s), 930 (w), 642 (m), 592 (m), 553 cm^{-1} (w); Raman (200 mW, 25 °C): $\tilde{\nu} = 2857$ (3), 2178/2142 (9), 1606/1592 (2), 1402 (5), 1330/1306 (1), 1001 (1), 882 (1), 642 (10), 611 (1), 230 (4), 140 cm^{-1} (3); ^{1}H NMR ([D$_6$]DMSO, 400 MHz, 25 °C): $\delta = 8.49$ ppm (s, CHO); ^{13}C NMR ([D$_6$]DMSO, 101 MHz, 25 °C): $\delta = 172.9$ (s, CHO), 123.4 ppm (s, CN); ^{14}N NMR ([D$_6$]DMSO, 28.9 MHz, 25 °C): $\delta = -190$ (s, $\Delta\nu^{1/2} = 1156$ Hz, CN), -245 ppm (s, $\Delta\nu^{1/2} = 1927$ Hz, N-CHO); MS (FAB$^-$, Xenon, 6 keV, *m*-NBA-matrix), *m/z* (%): 69 (24) [M]; elemental analysis: calcd (%) for C_2HKN_2O (108.14): C 22.21, H 0.93, N 25.90; found: C 21.92, H 1.29, N 26.51.

Ag$^+$fca$^-$: Sodium formylcyanoamide (0.50 g; 5.43 mmol) was slowly added to a solution of silver nitrate (0.90 g; 5.30 mmol) in H_2O (40 mL; acidified by 3 drops of conc. HNO_3) at 0 °C in a dark room. After stirring for 15 min at 0 °C, the Ag$^+$fca$^-$ was filtered and washed with H_2O (25 mL), ethanol, and diethyl ether. The Ag$^+$fca$^-$ was dried in vacuum for 30 min. Yield: 0.89 g (95 %); IR (ATR, 25 °C): $\tilde{\nu} = 2894$ (w), 2184 (s), 1614 (s), 1396 (w), 1292 (m), 1084 cm^{-1} (w); Raman (100 mW, 25 °C): $\tilde{\nu} = 2916$ (2), 2181 (10), 1598 (2), 1390 (2), 1319 (1), 634 (6), 607 (1), 556 (1), 236 cm^{-1} (3); elemental analysis: calcd (%) for C_2HAgN_2O (176.91): C 13.58, H 0.57, N 15.83; found: C 13.72, H 0.72, N 16.06.

Phfca: A solution of BrCN (2.12 g; 0.02 mol) in dried acetonitrile (20 mL) was added to a heavily stirred solution of potassium phenylformylamide (3.18 g; 0.02 mol) in dried acetonitrile (50 mL) at ambient temperature. After stirring for 16 h, the KBr was filtered and the solvent was removed in vacuum. Recrystallization from chloroform yielded Phfca (1.58 g; 54 %). M.p.: 55 °C; b.p.: 195 °C; IR (ATR, 25 °C): $\tilde{\nu} = 3066$ (w), 2953 (w), 2908 (w), 2265/2229 (m), 1664 (vs), 1592 (m), 1490 (s), 1386 (w), 1346 (m), 1182 (s), 1149 (s), 1125 (m), 1072 (m), 1012 (m), 1002 (w), 965 (w), 918 (w), 725 (s), 639 cm^{-1} (m); Raman (200 mW, 25 °C): $\tilde{\nu} = 3067$ (7), 2985 (8), 2906 (1), 2262/2237 (2), 1756 (4), 1596 (5), 1498 (0.5), 1438 (1), 1341 (3), 1341 (3), 1179 (1), 1160 (1), 1124 (0.5), 1026 (2), 1002 (10), 937 (1), 912 (0.5), 748 (3), 614 (1), 539 (3), 483 cm^{-1} (1); ^{1}H NMR ([D$_1$]CDCl$_3$, 400 MHz, 25 °C): $\delta = 9.02$ (s, 1 H, CHO), 7.50–7.18 ppm (m, 5 H, Ph); ^{13}C NMR ([D$_1$]CDCl$_3$, 101 MHz, 25 °C): $\delta = 163.5$ (s, CHO), 130.7 (s, Ph, ipso), 129.7 (s, Ph, para), 129.4 (s, Ph, meta), 127.3 (s, Ph, ortho), 116.3 ppm (s, CN); ^{14}N NMR ([D$_1$]CDCl$_3$, 28.9 MHz, 25 °C): $\delta = -159$ (s, $\Delta\nu^{1/2} = 445$ Hz, CN), -203 ppm (s, $\Delta\nu^{1/2} = 792$ Hz, N-CHO); MS (EI$^+$, 70 eV, >0.5 %), *m/z* (%): 146 (1) [M], 121 (100) [M$-$CN+H], 118 (5) [M$-$CO], 92 (9) [M$-$CN$-$CO], 77 (16) [M$-$N(CHO)CN]; elemental analysis: calcd (%) for $C_8H_6N_2O$ (146.15): C 65.75, H 4.14, N 19.17; found; C 65.86, H 4.25, N 18.92.

Phdca: A solution of BrCN (2.12 g; 0.02 mol) in dried acetonitrile (20 mL) was added to a heavily stirred solution of potassium phenylcyanoamide (3.12 g; 0.02 mol) in dried acetonitrile (50 mL) at ambient temperature. After stirring for 16 h, the KBr was filtered and the solvent was removed in vacuum. Recrystallization from chloroform yielded Phdca (1.67 g; 58 %). M.p.: 92 °C; b.p.: 187 °C; IR (ATR, 25 °C): $\tilde{\nu} = 3059$ (w), 2961 (w), 2264 (m), 2230 (s), 1563 (s), 1490 (vs), 1347 (s), 1262 (s), 1237 (vs), 1182 (m), 1025 (w), 1003 (w), 902 (w), 748 (s), 638 cm^{-1} (m); Raman (200 mW, 25 °C): $\tilde{\nu} = 3066$ (7), 2984 (3), 2262 (10), 2225 (2), 1592 (4), 1462 (1), 1240 (6), 1183 (2), 1035 (1), 1001 (7), 898 (1), 752 (1), 633 (2), 526 cm^{-1} (1); ^{1}H NMR ([D$_1$]CDCl$_3$, 400 MHz, 25 °C): $\delta = 7.53$–7.29 ppm (m, 5 H, Ph); ^{13}C NMR ([D$_1$]CDCl$_3$, 101 MHz, 25 °C): $\delta = 133.4$ (s, Ph, ipso), 130.4 (s, Ph, meta), 127.5 (s, Ph, para), 116.1 (s, Ph, ortho), 103.5 ppm (s, CN); ^{14}N NMR ([D$_1$]CDCl$_3$, 28.9 MHz, 25 °C): $\delta = -154$ (s, $\Delta\nu^{1/2} = 550$ Hz, CN), -323 ppm (s, $\Delta\nu^{1/2} = 852$ Hz, Ph-N); MS (EI$^+$, 70 eV, $>$ 5 %), *m/z* (%): 143 (100) [M], 117 (9) [M$-$CN], 91 (30) [M$-$2 CN], 77 (100) [M$-$N(CN)$_2$]; elemental analysis: calcd (%) for $C_8H_5N_3$ (143.15): C 67.13, H 3.52, N 29.35; found; C 67.44, H 3.42, N 29.64.

Na$^+$nca$^-$: A solution of sodium hydroxide (0.59 g; 14.8 mmol) in H_2O (5 mL) was added to a boiling suspension of *S*-methyl-*N*-nitroisothiourea (2.00 g; 14.8 mmol) in isopropanol (40 mL). After stirring for 40 min at this temperature, the reaction mixture was allowed to cool to ambient temperature and was subsequently neutralized with hydrochloric acid (2 N). After removal of the solvent, the residue was dried in vacuum. Recrystallization from acetone and drying in vacuum yielded Na$^+$nca$^-$ (1.44 g; 89 %). M.p.: 203 °C; $T_{\text{dec,onset}} = 254$ °C; IR (ATR, 25 °C): $\tilde{\nu} = 2196$ (s), 1450 (s), 1287 (vs), 1178/1168 (m), 984/967 (w), 776 (w), 764 (m), 545 (m), 511 cm^{-1} (m); Raman (200 mW, 25 °C): $\tilde{\nu} = 2192$ (10), 1466 (1), 1319 (2), 1181 (3), 967 (6), 774 (5), 610 (2), 547 (1), 515 (2), 230 (2), 135 cm^{-1} (3); ^{13}C NMR ([D$_6$]DMSO, 101 MHz, 25 °C): $\delta = 116.7$ ppm (s, CN); ^{14}N NMR ([D$_6$]DMSO, 28.9 MHz, 25 °C): $\delta = -2$ (s, $\Delta\nu^{1/2} = 23$ Hz, N-*N*O$_2$), -165 (s, $\Delta\nu^{1/2} = 407$ Hz, *N*-NO$_2$), -178 ppm (s, $\Delta\nu^{1/2} = 211$ Hz, CN); MS (FAB$^-$, Xenon, 6 keV, *m*-NBA-matrix), *m/z* (%): 86 (78) [M]; elemental analysis: calcd (%) for CN_3NaO_2 (109.02): C 11.02, N 38.54; found: C 10.78, N 38.03.

Li$^+$nca$^-$: A solution of lithium hydroxide (0.39 g; 16.3 mmol) in H_2O (5 mL) was added to a boiling suspension of *S*-methyl-*N*-nitroisothiourea (2.20 g; 16.3 mmol) in isopropanol (40 mL). After stirring for 40 min at this temperature, the reaction mixture was allowed to cool to ambient temperature and was subsequently neutralized with hydrochloric acid (2 N). After removal of the solvent, the residue was dried in vacuum. Recrystallization from acetone and drying in vacuum (4 d at 60 °C) yielded Li$^+$nca$^-$ (1.23 g; 81 %); $T_{\text{dec,onset}} = 215$ °C; IR (ATR, 25 °C): $\tilde{\nu} = 2211$ (s), 1438 (s), 1276 (vs), 1173 (m), 972 (w), 774 (w), 760 (w), 536 (m), 520 cm^{-1} (m); Raman (200 mW, 25 °C): $\tilde{\nu} = 2229$ (10), 1540 (2), 1290 (1), 1173 (5), 982 (5), 778 (3), 622 (1), 537 (1), 506 (1), 227 (4), 151 cm^{-1} (5); ^{13}C NMR ([D$_6$]DMSO, 101 MHz, 25 °C): $\delta = 116.7$ ppm (s, CN); ^{14}N NMR ([D$_6$]DMSO, 28.9 MHz, 25 °C): $\delta = -2$ (s, $\Delta\nu^{1/2} = 23$ Hz, N-*N*O$_2$), -165 (s, $\Delta\nu^{1/2} = 407$ Hz, *N*-NO$_2$), -178 ppm (s, $\Delta\nu^{1/2} = 211$ Hz, CN). MS (FAB$^-$, Xenon, 6 keV, *m*-NBA-matrix), *m/z* (%): 86 (80) [M]; elemental analysis: calcd (%) for $CLiN_3O_2$ (92.97): C 12.92, N 45.20; found: C 12.27, N 44.53.

Cs$^+$nca$^-$: A solution of cesium hydroxide monohydrate (1.31 g; 7.80 mmol) in H_2O (5 mL) was added to a boiling suspension of *S*-methyl-*N*-nitroisothiourea (1.06 g; 7.79 mmol) in isopropanol (40 mL). After 40 min stirring at this temperature, the reaction mixture was allowed to cool to ambient temperature and was subsequently neutralized with hydrochloric acid (2 N). After removal of the solvent, the residue was dried in vacuum. Recrystallization from acetone and drying in vacuum (1 d at 60 °C) yielded Cs$^+$nca$^-$ (1.57 g; 92 %). M.p.: 93 °C, $T_{\text{dec,onset}} = 312$ °C; IR (ATR, 25 °C): $\tilde{\nu} = 2178$ (vs), 1430 (s), 1260 (s), 1160 (s), 960 (m), 772 (m), 764 (m), 548 (m), 512 cm^{-1} (m); Raman (200 mW, 25 °C): $\tilde{\nu} = 2184$ (10), 1441 (1), 1257 (1), 1166 (3), 958 (2), 766 (5), 599 (1), 509 (1), 226 cm^{-1} (3); ^{13}C NMR ([D$_6$]DMSO, 101 MHz, 25 °C): $\delta = 116.7$ ppm (s, CN); ^{14}N NMR ([D$_6$]DMSO, 28.9 MHz, 25 °C): $\delta = -2$ (s, $\Delta\nu^{1/2} = 23$ Hz, N-*N*O$_2$), -165 (s, $\Delta\nu^{1/2} = 407$ Hz, *N*-NO$_2$), -178 ppm (s, $\Delta\nu^{1/2} = 211$ Hz, CN); MS (FAB$^-$, Xenon, 6 keV, *m*-NBA-matrix), *m/z* (%): 86 (77) [M]; elemental analysis: calcd (%) for $CCsN_3O_2$ (218.94): C 5.49, N 19.19; found; C 5.24, N 18.84.

Ba^{2+}(nca$^-$)$_2$: Barium hydroxide octahydrate (1.53 g; 4.85 mmol) was added to a boiling suspension of *S*-methyl-*N*-nitroisothiourea (1.31 g; 9.69 mmol) in isopropanol (40 mL) and H_2O (60 mL) in five portions (time interval 1.5 h). After stirring for 3 h at this temperature, the reaction mixture was allowed to cool down to ambient temperature and was subsequently neutralized with hydrochloric acid (2 N). After removal of the solvent, the residue was dried in vacuum. Recrystallization from acetone and drying in vacuum (1 d at 60 °C) yielded Ba^{2+}(nca$^-$)$_2$ (1.08 g; 72 %). $T_{\text{dec,onset}} = 293$ °C; IR (ATR, 25 °C): $\tilde{\nu} = 2212$ (s), 1418 (s), 1276 (vs), 1172 (m), 979 (m), 764 (m), 528 (m), 509 cm^{-1} (m); Raman (200 mW, 25 °C): $\tilde{\nu} = 2219$ (9), 1529 (0.5), 1299 (1), 1177 (8), 982 (10), 766 (6), 623 (3), 532 (1), 498 (2), 221 (5), 143 cm^{-1} (2); ^{13}C NMR ([D$_6$]DMSO, 101 MHz, 25 °C): $\delta = 116.7$ ppm (s, CN); ^{14}N NMR ([D$_6$]DMSO, 28.9 MHz, 25 °C): $\delta = -2$ (s, $\Delta\nu^{1/2} = 23$ Hz, N-*N*O$_2$), -165 (s, $\Delta\nu^{1/2} = 407$ Hz, *N*-NO$_2$), -178 ppm (s, $\Delta\nu^{1/2} = 211$ Hz, CN). MS (FAB$^-$, Xenon, 6 keV, *m*-NBA-matrix), *m/z* (%): 86 (81) [M]; elemental analysis: calcd (%) for $C_2BaN_6O_4$ (309.38): C 7.76, N 27.16; found: C 7.53, N 26.74.

EMIM$^+$dfa$^-$: Potassium diformylamide (0.68 g; 6.12 mmol) was added to a solution of 1-ethyl-3-methylimidazolium tetrafluoroborate (1.13 g; 5.71 mmol) in dried methanol (50 mL) at RT. After stirring for 20 h at RT, the reaction mixture was filtered. Removal of the solvent in vaccum, followed by a specific drying procedure (see Scheme 6) and drying for 7 d in vacuum (10^{-3} Torr), yielded a red-brown ionic liquid (0.94 g; 90 %). M.p.: -18 °C; $T_{\text{dec,onset}} = 213$ °C; IR (ATR, 25 °C): $\tilde{\nu} = 3151$ (w), 3084 (m), 2982 (w), 2863 (w), 1696 (m), 1554 (vs), 1470 (w), 1269 (s), 1232 (m), 1170 (s), 1052 (s), 732 (m), 623 cm^{-1} (m); Raman (200 mW, 25 °C): $\tilde{\nu}=3073$ (6), 2966 (10), 2860 (1), 1682 (8), 1575 (1), 1455 (5), 1421 (7), 1338 (5), 1097 (1), 1023 (5), 959 (1), 589 cm^{-1} (8); ^{1}H NMR ([D$_6$]DMSO, 400 MHz, 25 °C): $\delta=8.95$ ppm (N-C*H*O); ^{13}C NMR ([D$_6$]DMSO, 101 MHz, 25 °C): $\delta=181.3$ ppm (N-*C*HO); ^{14}N NMR ([D$_6$]DMSO, 28.9 MHz, 25 °C): $\delta=-128$ ppm (*N*-CHO); elemental analysis: calcd (%) for $C_8H_{13}N_3O_2$ (183.21): C 52.45, H 7.15, N 22.94; found; C 52.12, H 6.84, N 22.45.

EMIM$^+$fca$^-$: Potassium formylcyanoamide (0.65 g; 6.01 mmol) was added to a solution of 1-ethyl-3-methylimidazolium tetrafluoroborate (1.16 g; 5.86 mmol) in dried methanol (50 mL) at RT. After stirring for 20 h at RT, the reaction mixture was filtered. Removal of the solvent in vaccum, followed by a specific drying procedure (see Scheme 6) and drying for 7 d in vacuum (10^{-3} Torr), yielded a colorless ionic liquid (1.01 g; 96 %). M.p.: −5 °C; $T_{\text{dec,onset}}=218$ °C; IR (ATR, 25 °C): $\tilde{\nu}=3143$ (m), 3067 (s), 2861 (w), 2148 (s), 1565 (vs), 1304 (m), 1168 (vs), 829 (m), 754 (m), 700 (w), 646 (w), 619 cm^{-1} (m); Raman (200 mW, 25 °C): $\tilde{\nu}=$ 2859 (7), 2142 (6), 1570 (3), 1447 (5), 1423 (10), 1387 (6), 1342 (5), 1253 (3), 1096 (4), 1025 (8), 961 (4), 833 (2), 702 (3), 600 cm^{-1} (6); ^{1}H NMR ([D$_6$]DMSO, 400 MHz, 25 °C): $\delta=8.49$ ppm (N-C*H*O); ^{13}C NMR ([D$_6$]DMSO, 101 MHz, 25 °C): $\delta=172.9$ (N-*C*HO), 123.4 ppm (N-*C*N); ^{14}N NMR ([D$_6$]DMSO, 28.9 MHz, 25 °C): $\delta=-190$ (N-C*N*), −245 ppm (*N*-CHO); elemental analysis: calcd (%) for $C_8H_{12}N_4O$ (180.21): C 53.32, H 6.71, N 31.09; found; C 53.07, H 6.24, N 30.62.

EMIM$^+$nca$^-$: Potassium nitrocyanoamide (0.83 g; 6.63 mmol) was added to a solution of 1-ethyl-3-methylimidazolium tetrafluoroborate (1.25 g; 6.31 mmol) in dried methanol (50 mL) at RT. After stirring for 20 h at RT, the reaction mixture was filtered. Removal of the solvent in vaccum, followed by a specific drying procedure (see Scheme 6) and drying for 7 d in vacuum (10^{-3} Torr), yielded a colorless glass (1.21 g; 97 %). M.p.: 27 °C; $T_{\text{dec,onset}}=225$ °C; IR (ATR, 25 °C): $\tilde{\nu}=3150$ (w), 3110 (m), 2986 (w), 2168 (s), 1572 (m), 1424 (s), 1258 (vs), 1166 (s), 1152 (m), 951 (w), 842 (w), 760 (w), 701 (w), 647 (w), 621 cm^{-1} (w); Raman (200 mW, 25 °C): $\tilde{\nu}=3171$ (2), 2988 (5), 2962 (6), 2945 (6), 2171 (10), 1570 (1), 1450 (4), 1426 (6), 1386 (3), 1335 (3), 1259 (2), 1153 (6), 1089 (4), 1023 (5), 953 (6), 762 (8), 704 (1), 598 (5), 502 cm^{-1} (2); ^{13}C NMR ([D$_6$]DMSO, 101 MHz, 25 °C): $\delta=116.7$ ppm (N-*C*N); ^{14}N NMR ([D$_6$]DMSO, 28.9 MHz, 25 °C): $\delta=-2$ (N-*N*O$_2$), −165 (*N*-NO$_2$), −178 ppm (N-C*N*); elemental analysis: calcd (%) for $C_7H_{11}N_5O_2$ (197.20): C 42.64, H 5.62, N 35.51; found: C 42.07, H 5.14, N 34.89.

BMIM$^+$dfa$^-$: Potassium diformylamide (1.09 g; 9.81 mmol) was added to a solution of 1-*n*-butyl-3-methylimidazolium tetrafluoroborate (2.04 g; 9.03 mmol) in dried methanol (50 mL) at RT. After stirring for 20 h at RT, the reaction mixture was filtered. Removal of the solvent in vaccum, followed by a specific drying procedure (see Scheme 6) and drying for 7 d in vacuum (10^{-3} Torr), yielded a red-brown ionic liquid (1.74 g; 91 %). M.p.: −26 °C; $T_{\text{dec,onset}}=221$ °C; IR (ATR, 25 °C): $\tilde{\nu}=3157$ (m), 3114 (m), 2963 (m), 2938 (m), 2876 (m), 1696 (s), 1561 (vs), 1466 (w), 1386 (w), 1272 (m), 1169 (s), 1049 (vs), 1036 (vs), 849 (w), 752 (w), 732 (w), 652 (w), 623 (m); Raman (200 mW, 25 °C): $\tilde{\nu}=2967$ (8), 2875 (6), 1687 (7), 1569 (7), 1451 (8), 1420 (10), 1390 (8), 1342 (9), 1117 (7), 1025 (9), 767 (8), 589 cm^{-1} (9); ^{1}H NMR ([D$_6$]DMSO, 400 MHz, 25 °C): $\delta=$ 8.95 ppm (N-C*H*O); ^{13}C NMR ([D$_6$]DMSO, 101 MHz, 25 °C): $\delta=$ 181.3 ppm (N-*C*HO); ^{14}N NMR ([D$_6$]DMSO, 28.9 MHz, 25 °C): $\delta=$ −128 ppm (*N*-CHO); elemental analysis: calcd (%) for $C_{10}H_{17}N_3O_2$ (211.26): C 56.85, H 8.11, N 19.89; found: C 56.37, H 7.86, N 19.28.

BMIM$^+$fca$^-$: Potassium formylcyanoamide (1.07 g; 9.89 mmol) was added to a solution of 1-*n*-butyl-3-methylimidazolium tetrafluoroborate (2.13 g; 9.42 mmol) in dried methanol (50 mL) at RT. After stirring for 20 h at RT, the reaction mixture was filtered. Removal of the solvent in vaccum, followed by a specific drying procedure (see Scheme 6) and drying for 7 d in vacuum (10^{-3} Torr), yielded a colorless glass (1.84 g; 94 %). M.p.: 32 °C; $T_{\text{dec,onset}}=227$ °C; IR (ATR, 25 °C): $\tilde{\nu}=3143$ (m), 3074 (s), 2960 (s), 2936 (s), 2873 (m), 2150 (s), 1571 (vs), 1463 (m), 1381 (w), 1305 (s), 1167 (s), 1066 (w), 960 (w), 831 (m), 753 (m), 652 (m), 621 cm^{-1} (m); Raman (200 mW, 25 °C): $\tilde{\nu}=3125$ (2), 3081 (3), 2953 (9), 2908 (8), 2867 (6), 2145 (2), 1566 (2), 1455 (4), 1416 (10), 1375 (4), 1333 (4), 1302 (2), 1136 (2), 1092 (3), 1052 (3), 1016 (5), 887 (2), 837 (2), 701 (3), 604 cm^{-1} (3); ^{1}H NMR ([D$_6$]DMSO, 400 MHz, 25 °C): $\delta=8.49$ ppm (N-C*H*O); ^{13}C NMR ([D$_6$] DMSO, 101 MHz, 25 °C): $\delta=172.9$ (N-*C*HO), 123.4 ppm (N-*C*N); ^{14}N NMR ([D$_6$]DMSO, 28.9 MHz, 25 °C): $\delta=-190$ (N-C*N*), −245 ppm (*N*-CHO); elemental analysis: calcd (%) for $C_{10}H_{16}N_4O$ (208.26): C 57.67, H 7.74, N 26.90; found: C 57.35, H 7.59, N 26.44.

BMIM$^+$nca$^-$: Potassium nitrocyanoamide (1.12 g; 8.95 mmol) was added to a solution of 1-*n*-butyl-3-methylimidazolium tetrafluoroborate (1.89 g; 8.36 mmol) in dried methanol (50 mL) at RT. After stirring for 20 h at RT, the reaction mixture was filtered. Removal of the solvent in vaccum, followed by a specific drying procedure (see Scheme 6) and drying for 7 d in vacuum (10^{-3} Torr), yielded a colorless ionic liquid (1.74 g; 91 %). M.p.: −6 °C; $T_{\text{dec,onset}}=234$ °C; IR (ATR, 25 °C): $\tilde{\nu}=3149$ (m), 3109 (m), 2961 (m), 2936 (m), 2169 (s), 1572 (m), 1425 (s), 1260 (vs), 1165 (s), 950 (w), 844 (w), 760 (w), 650 cm^{-1} (vs); Raman (200 mW, 25 °C): $\tilde{\nu}=3164$ (2), 3122 (1), 2962 (7), 2941 (6), 2172 (10), 1566 (1), 1447 (3), 1418 (4), 1387 (2), 1341 (2), 1265 (1), 1153 (3), 1116 (1), 1024 (4), 953 (5), 763 (5), 625 (1), 592 (3), 502 cm^{-1} (1); ^{13}C NMR ([D$_6$] DMSO, 101 MHz, 25 °C): $\delta=116.7$ ppm (N-*C*N); ^{14}N NMR ([D$_6$]DMSO, 28.9 MHz, 25 °C): $\delta=-2$ (N-*N*O$_2$), −165 (*N*-NO$_2$), −178 ppm (N-C*N*); elemental analysis: calcd (%) for $C_9H_{15}N_5O_2$ (225.25): C 47.99, H 6.71, N 31.09; found: C 47.53, H 6.64, N 30.74.

HMIM$^+$dfa$^-$: Potassium diformylamide (0.92 g; 8.28 mmol) was added to a solution of 1-*n*-hexyl-3-methylimidazolium tetrafluoroborate (1.95 g; 7.67 mmol) in dried methanol (50 mL) at RT. After stirring for 20 h at RT, the reaction mixture was filtered. Removal of the solvent in vaccum, followed by a specific drying procedure (see Scheme 6) and drying for 7 d in vacuum (10^{-3} Torr), yielded a red-brown ionic liquid (1.69 g (92 %). M.p.: −41 °C; $T_{\text{dec,onset}}=228$ °C; IR (ATR, 25 °C): $\tilde{\nu}=3153$ (w), 3105 (w), 2958 (m), 2932 (m), 2860 (m), 1697 (m), 1558 (vs), 1467 (w), 1380 (w), 1271 (m), 1169 (m), 1053 (s), 732 (w), 623 cm^{-1} (w); Raman (200 mW, 25 °C): $\tilde{\nu}=2935$ (7), 2858 (6), 1683 (9), 1566 (9), 1415 (10), 1388 (9), 1336 (10), 1119 (8), 1027 (9), 898 (8), 766 (9), 588 (9), 419 cm^{-1} (9); ^{1}H NMR ([D$_6$]DMSO, 400 MHz, 25 °C): $\delta=8.95$ ppm (N-C*H*O); ^{13}C NMR ([D$_6$]DMSO, 101 MHz, 25 °C): $\delta=181.3$ ppm (N-*C*HO); ^{14}N NMR ([D$_6$]DMSO, 28.9 MHz, 25 °C): $\delta=-128$ ppm (*N*-CHO); elemental analysis: calcd (%) for $C_{12}H_{21}N_3O_2$ (239.32): C 60.23, H 8.84, N 17.56; found: C 59.94, H 8.52, N 17.09.

HMIM$^+$fca$^-$: Potassium formylcyanoamide (0.97 g; 8.97 mmol) was added to a solution of 1-*n*-hexyl-3-methylimidazolium tetrafluoroborate (2.13 g; 8.38 mmol) in dried methanol (50 mL) at RT. After stirring for 20 h at RT, the reaction mixture was filtered. Removal of the solvent in vaccum, followed by a specific drying procedure (see Scheme 6) and drying for 7 d in vacuum (10^{-3} Torr), yielded a colorless ionic liquid (1.88 g; 95 %). M.p.: −15 °C; $T_{\text{dec,onset}}=231$ °C; IR (ATR, 25 °C): $\tilde{\nu}=3146$ (w), 3094 (w), 2956 (m), 2931 (m), 2859 (w), 2147 (s), 1584 (vs), 1466 (w), 1380 (w), 1303 (s), 1167 (m), 1065 (w), 961 (w), 830 (w), 760 (w), 623 cm^{-1} (w); Raman (200 mW, 25 °C): $\tilde{\nu}=2960$ (10), 2940 (9), 2862 (7), 2445 (8), 2156 (7), 1576 (2), 1417 (5), 1389 (5), 1310 (4), 1024 (5), 964 (2), 832 (2), 634 cm^{-1} (3); ^{1}H NMR ([D$_6$]DMSO, 400 MHz, 25 °C): $\delta=$ 8.49 ppm (N-C*H*O); ^{13}C NMR ([D$_6$]DMSO, 101 MHz, 25 °C): $\delta=172.9$ (N-*C*HO), 123.4 ppm (N-*C*N); ^{14}N NMR ([D$_6$]DMSO, 28.9 MHz, 25 °C): $\delta=-190$ (N-C*N*), −245 ppm (*N*-CHO); elemental analysis: calcd (%) for $C_{12}H_{20}N_4O$ (236.32): C 60.99, H 8.53, N 23.71; found: C 60.34, H 8.27, N 23.42.

HMIM$^+$nca$^-$: Potassium nitrocyanoamide (1.26 g; 10.1 mmol) was added to a solution of 1-*n*-hexyl-3-methylimidazolium tetrafluoroborate (2.51 g; 9.88 mmol) in dried methanol (50 mL) at RT. After stirring for 20 h at RT, the reaction mixture was filtered. Removal of the solvent in vaccum, followed by a specific drying procedure (see Scheme 6) and drying for 7 d in vacuum (10^{-3} Torr), yielded a colorless ionic liquid (2.40 g; 96 %). M.p.: −38 °C; $T_{\text{dec,onset}}=239$ °C; IR (ATR, 25 °C): $\tilde{\nu}=3148$ (w), 3108 (w), 2956 (m), 2931 (m), 2860 (w), 2168 (s), 1571 (w), 1424 (s), 1259 (vs), 1165 (m), 951 (w), 845 (w), 760 (w), 622 cm^{-1} (w); Raman (200 mW, 25 °C): $\tilde{\nu}=2962$ (8), 2941 (7), 2520 (5), 2171 (10), 1569 (1), 1417 (4), 1341 (2), 1261 (1), 1151 (3), 1025 (3), 955 (4), 764 cm^{-1} (6); ^{13}C NMR ([D$_6$]DMSO, 101 MHz, 25 °C): $\delta=116.7$ ppm (N-*C*N); ^{14}N NMR ([D$_6$]DMSO, 28.9 MHz, 25 °C): $\delta=-2$ (N-*N*O$_2$), −165 (*N*-NO$_2$), −178 ppm (N-C*N*); elemental analysis: calcd (%) for $C_{11}H_{19}N_5O_2$ (253.31): C 52.16, H 7.56, N 27.65; found; C 51.89, H 7.21, N 27.18.

HMIM$^+$dca$^-$: Potassium dicyanoamide (0.95 g; 9.04 mmol) was added to a solution of 1-*n*-hexyl-3-methylimidazolium tetrafluoroborate (2.25 g; 8.86 mmol) in of dried methanol (50 mL) at RT. After stirring for 20 h at RT, the reaction mixture was filtered. Removal of the solvent in vaccum, followed by a specific drying procedure (see Scheme 6) and drying for 7 d in vacuum (10^{-3} Torr), yielded a colorless ionic liquid (2.03 g; 98 %). M.p.: −48 °C; $T_{\mathrm{dec,onset}} = 246$ °C; IR (ATR, 25 °C): $\tilde{\nu} = 3100$ (w), 2956 (w), 2931 (w), 2860 (w), 2228 (s), 2192 (s), 2125 (vs), 1572 (m), 1466 (w), 1305 (m), 1166 (m), 753 (w), 651 (w), 622 $\mathrm{cm^{-1}}$ (w); Raman (200 mW, 25 °C): $\tilde{\nu} = 3090$ (1), 2958 (6), 2935 (5), 2873 (4), 2192 (10), 2135 (1), 1570 (1), 1441 (2), 1418 (3), 1387 (1), 1340 (1), 1311 (1), 1115 (1), 1023 (3), 896 (1), 665 $\mathrm{cm^{-1}}$ (2); ^{13}C NMR ([D$_6$]DMSO, 101 MHz, 25 °C): $\delta = 118.9$ ppm (N-*C*N); ^{14}N NMR ([D$_6$]DMSO, 28.9 MHz, 25 °C): $\delta = -229$ (N-C*N*), −368 ppm (*N*-CN); elemental analysis: calcd (%) for $C_{12}H_{19}N_5$ (233.32): C 61.77, H 8.21, N 30.02; found: C 61.46, H 7.93, N 29.69.

Computational Details

Our goal was to compare the structures and energetics of different isomers. Therefore it was important to carry out the calculations in such a way that the results could be compared reliably with each other. The structural and vibrational data of all considered species and adducts were calculated by using hybrid density functional theory (B3LYP) with the program package Gaussian03.[75] A 6–31G(d,p) standard basis set was applied for all atoms. The computed geometrical parameters and frequency data can be obtained from the authors or supporting information.

NBO analyses[48–51] were carried out to investigate the bonding in all molecules at the B3LYP level utilizing the optimized B3LYP geometry.

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