N-[(2-Naphthyloxy)methyl]benzazoles: Synthesis and Investigation by X-ray Analysis and by Semiempirical MO Calculations

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The crystal structures of 1-[(2-naphthyloxy)methyl]-1H-benzotriazole (4) and -1H-benzimidazole (8) and the 3-metho-quaternary iodide 9 derived from 8 are reported. The experimentally determined geometries are compared with the corresponding results from MNDO, AM1, and PM3 calculations. Remarkably, the crystal structures differ significantly from those calculated by AM1 as most stable. — Thus, conformations of 9 (from the crystal structure) and 9a (the most stable AM1 structure) differ in energy by ca. 3.5 kcal/mol. This stabilization of 9a is due to the anomeric effect which cannot be expressed in conformation 9. Calculations of the alternative cleavage of the methyl or of the naphthyloxymethyl cation (Figure 6) clarify discrepancies between the experimental and the calculated bond lengths.

We are highly interested in the synthetic possibilities of systems containing an electrophilic carbon atom activated by an electron donor group and directly linked to the nitrogen atom of a heterocycle. The heterocycle can be either a neutral species (benzotriazole[1]) or a cation (pyridinium[2]). For example, it has been recently demonstrated[3] that reactions between Grignard reagents and N-(α-benzotriazol-1-ylalkyl)arylamines readily yield the corresponding branched secondary amines by displacement of the benzotriazole moiety (Scheme 1).

Scheme 1
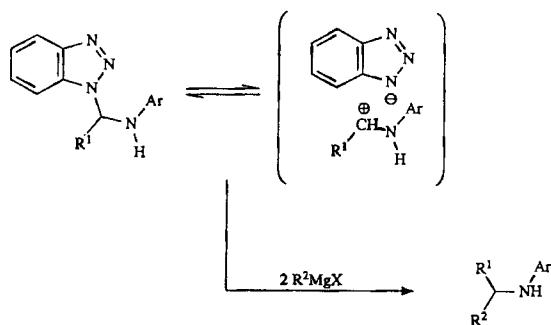
Although we have now been able to synthesize ethers by a similar reaction sequence from 1-[α-(alkoxy)alkyl)benzotriazoles[4], several difficulties were initially encountered in this ether synthesis project. This prompted us to synthesize other derivatives of the type het-CH₂-OR (vide infra) in order to investigate their structure and to search for a theoretical background to our observation of reactivity differences. Indeed, beside net charge on the electrophilic carbon

atom and thermodynamic considerations, we previously observed that the bond length between the carbon atom at the reactive center and the nitrogen atom of the heterocycle is a useful criterion for the reactivity towards nucleophilic reagents[2b].

To better understand the effect of an additional nitrogen atom, and the effect of quaternization, on the bonding in systems of type het−CH₂−OR, we decided to investigate the geometry of representative examples of this class of compounds in which "het" was neutral benzimidazole and benzotriazole and also a corresponding cationic analog. The present paper describes the results of these investigations.

Syntheses

We prepared 1-[(2-naphthyloxy)methyl]-1H-benzotriazole 4 and 1-[(2-naphthyloxy)methyl]-1H-benzimidazole (8, obtained as a hemihydrate) by classical routes: hydroxymethylation of the heterocycle followed by treatment with thionyl chloride and then with sodium 2-naphthoxide (Scheme 2). Quaternization of the benzimidazole derivative to give 1-methyl-3-[(2-naphthyloxy)methyl]-1H-benzimidazolium iodide (9) was readily achieved with methyl iodide (Scheme 2), the benzotriazole derivative could not be methylated under the same experimental conditions.
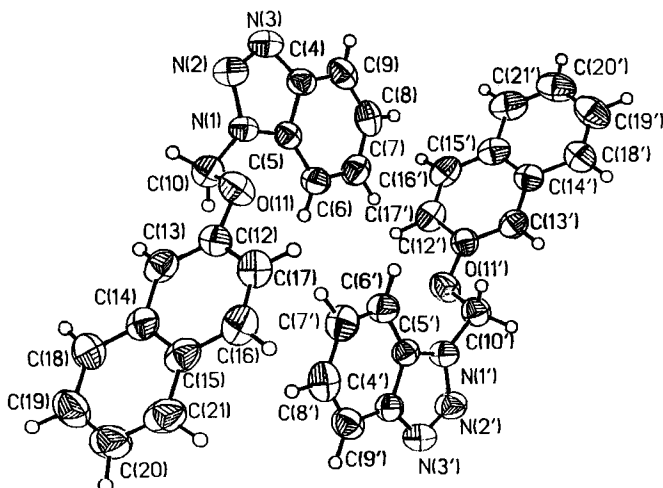
Crystal Structures

The crystal data for the three compounds 4, 8, and 9 are collected in Table 1. The final positional parameters are presented in Tables 2, 3, and 4. Selected distances and angles together with the results from the semiempirical calculations are given in Tables 5, 6, and 7. A complete set of distances and angles is available.

Scheme 2
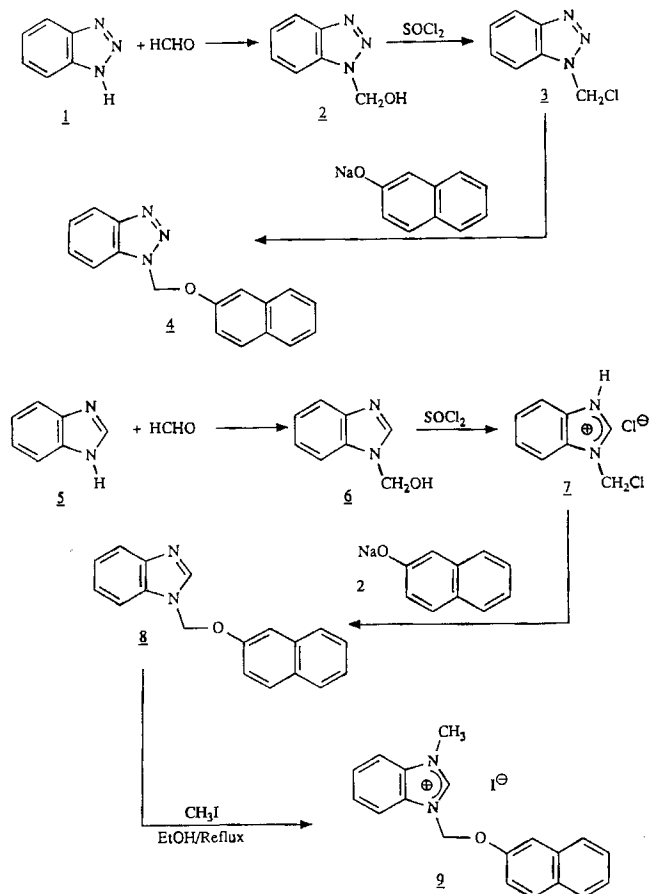
In all three compounds we have a (2-naphthyloxy)methyl group bonded to three different benzazoles. The naphthyl group is constant in all three structures and provides an interesting internal check on the accuracy of the determinations. Assuming *mm* symmetry we calculated average C−C dimensions of 1.404(9), 1.359(8), 1.416(9), and 1.414(9) Å compared to the corresponding values reported for naphthalene of 1.415, 1.378, 1.426, and 1.426 (all ±0.002

Å[5]). Our values are all slightly smaller, because rigid body corrections were not applied.

The dimensions of the three different benzazoles are similar to those reported elsewhere. The average values of N(1)−N(2) and N(2)−N(3) are 1.353(9) Å and 1.306(9) Å in various 1-substituted benzotriazoles[6,7] and are in good agreement with our values. Replacement of N(2) by the isoelectronic CH group does not produce a significant change in the bond length, i.e. N(1)−C(2) is 1.358(2) Å and C(2)−N(3) is 1.304(2) Å in **8**. However, the formation of a cation in **9** by the methyl group at N(3) makes the two C−N distances slightly shorter and equal [N(1)−C(2) is 1.326(6) Å and C(2)−N(3) is 1.325(6) Å]. In summary the various 1-substituted benzazoles have dimensions not significantly different from similar compounds reported in the literature.
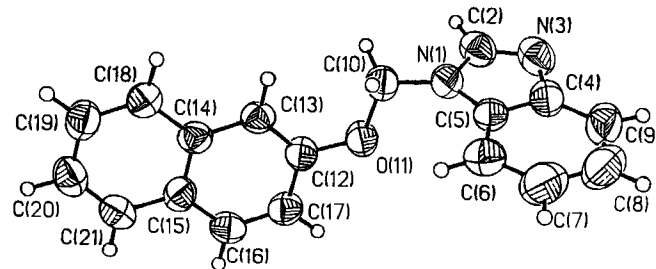
Figure 2. A view of a molecule of **8** in the crystal
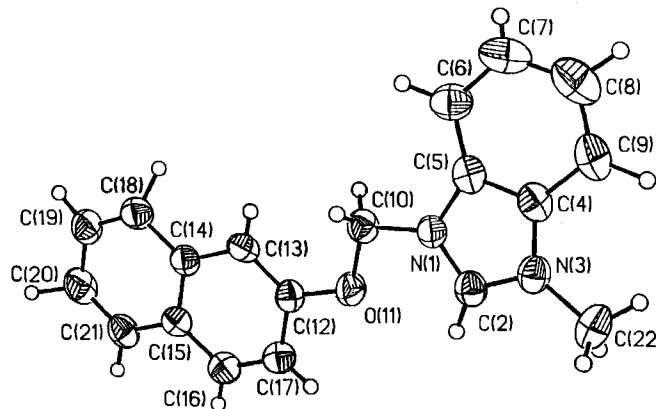
Figure 3. A view of the cation of **9** in the crystal

Semiempirical Calculations and Comparison with the X-ray Results

Our previous results on the substituent dependence of the bond lengths in N-heteroaromatic systems were based on **MNDO** calculations of substituted *N*-alkylpyridinium salts[2b].

We now consider the applicability of these results to the benzotriazole and benzimidazole ring systems, specifically to compounds **4, 8,** and **9**. Simultaneously, we have tested MNDO[8], AM1[9], and PM3[10] to find the most suitable semiempirical method for such investigations. The results are gathered in Tables 5−7 and Figure 4.

To compare the quality of the three semiempirical methods, the dihedral angles N3−C2−N1−C10, C2−N1−C10−O11, N1−C10−O11−C12, and C10−O11−C12−

Figure 1. A view of the two molecules in the crystal of **4**

C13 of **9** were fixed according to the X-ray crystallographic data[11]. Similar conditions were applied to compounds **4** and **8** (see Tables 5 and 6).

This comparison of the calculated and the experimental bond lengths and angles shows that AM1 (followed by PM3) gives better results than the MNDO method. All the methods described the geometry of the carbocyclic rings satisfactorily. Rather large discrepancies are shown for the heterocyclic parts of the molecules. In particular, AM1 and also MNDO calculate the bond C4−C5 (the annulation of the heteroatoms to the benzene ring) as too long. A similar conclusion holds for the N3−C22 bond to the methyl group of salt **9**. The exocyclic unit N1−C10−O11−C12 which is of special interest in the present study is described best by AM1. The following discussion applies to the AM1 results.

Both in the crystal structure and also in the structures calculated by AM1 for **8** and **9**, it is seen that the bond N1−C10 is lengthened by quaternization at the nitrogen atom N3, with a simultaneous shortening of the bond C10−O11. In principle, two different electronic effects could be responsible for this. On the one hand, the interaction of an oxygen electron pair with a σ* orbital of the N1−C10 bond (anomeric effect[2b]) causes bond lengthening. However, for this a suitable conformation of the naphthyloxymethyl group is required.

On the other hand, the electron density in **9** in the portion of the molecule under consideration is reduced in comparison to **8** because of the quaternization at N3. The altered bond length relationships are emphasized by the structural characteristics of the group that could later act as a cationic leaving group, i.e. the naphthyloxymethyl cation. We have called this effect "bond lengthening by cation formation (BLCF)"[12,13a,b]. This BLCF effect is obvious on comparison of the crystal structures of **8** and **9**. Any stabilization by the anomeric effect is practically eliminated for **9** because the two ring systems are almost coplanar. Hence, the lengthening of the N1−C10 bond and the shortening of the C10−O11 bond must overhelmingly be due to the BLCF effect. This is again shown by calculated ΔH_f values of the two different conformations of **9**. The crystal structure conformation of **9** is 3.5 kcal/mol less stable than its most stable conformation (see Table 5). As expected, the latter (which is stabilized by the anomeric effect) shows a slightly longer N1−C10 bond length in comparison to **9** [Table 5, 1.461 Å in comparison with 1.452 Å of **9**], and a slightly shorter C10−O11 bond length (1.412 Å in comparison with 1.429 Å of **9**).

For the most stable conformation, both effects act in the same direction. These small differences indicate that for both conformations of **9** the BLCF effect is most important.

Thus, crystal-packing effects cause for **9** and, to a somewhat lesser extent, for **4** and **8** conformations which can be quantitatively differentiated from those of the gas phase.

Especially significant is the deviation of the calculated N3−C22 bond length from the experimental result. In the *N*-alkylpyridinium series, such N⊕−C(alkyl) bond lengths are particularly well reproduced using AM1[14]. This finding was the stimulus for the calculation of the energy profiles of

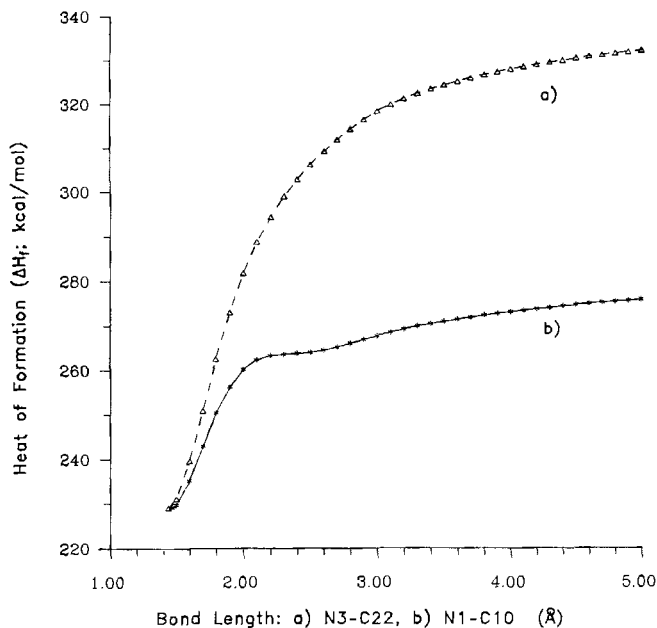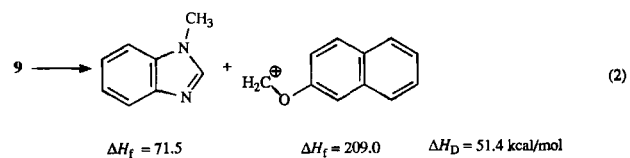the methyl and napthyloxymethyl groups for their loss from **9** as given in Figure 4[15].

Figure 4. Energy profiles for the dissociation of **9**: a) see eq. (1), b) see eq. (2)

The lengthening of the N3−C22 bond, from 1.436 Å to the value of 1.477 Å, found in the crystal structure, leads to a very small increase in the ΔH_f values of 0.7 kcal/mol. A comparable result is found by the lengthening of the N1−C10 bond length. The stretching of this bond type, energetically inexpensive up to a value of ca. 1.7 Å, in a crystal structure has consequences for both molecular groups. Significant differences become apparent as the N−C distances lengthen: the curves for N1−C10 and for N3−C22 energy profiles are then differentiated both quantitatively and qualitatively. For the loss of a methyl cation, the energy increases continuously until dissociation; by contrast, for the loss of a naphthyloxymethyl cation, the energy initially changes little with distance and begins to increase markedly only at around 2.7 Å. This is possibly due to the existence of a weakly stabilized ion-molecule complex[16].

The end points of these two energy profiles differ drastically. In each case they characterize the sum of the energy of the carbocation so formed and the neutral *N*-substituted benzimidazole. The dissociation energy ΔH_D calculated from equations (1) and (2) indicate that the complete dissociation of the naphthyloxymethyl group from **9** in the sense of a

$$\mathbf{9} \longrightarrow \mathbf{8} \quad + \quad CH_3^{\oplus} \tag{1}$$

$$\Delta H_f = 252.4 \qquad \Delta H_D = 110.4 \text{ kcal/mol}$$

$$\Delta H_f = 71.5 \qquad \Delta H_f = 209.0 \qquad \Delta H_D = 51.4 \text{ kcal/mol}$$
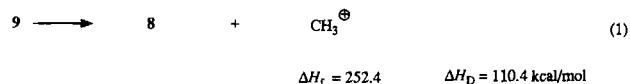
gas-phase S_N1 reaction should be significantly easier than that of the methyl group.

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Experimental

M.p.: Hot-stage microscope. ^{1}H NMR: Varian EM-360L (60 MHz); ^{13}C NMR: Varian XL-200 (50 MHz); tetramethylsilane as the internal reference. — Elemental analyses were carried out under the supervision of Dr. R. W. King, University of Florida.

Compounds **1** and **5** were commercial specimens (Aldrich). Compounds **2**[17], **3**[17], **6**[18], and **7**[19] were prepared as described in the literature and had melting points in agreement with the reported values.

1-[(2-Naphthyloxy)methyl]-1H-benzotriazole (**4**): 1-(Chloromethyl)-1H-benzotriazole (**3**; 1.67 g, 10 mmol) and sodium 2-naphthoxide (1.66 g, 10 mmol; prepared from sodium and 2-hydroxynaphthalene in refluxing toluene) were heated in ethanol (25 ml) to reflux for 6 h. After evaporation of the solvent under reduced pressure, water was added to the residue, and the precipitate was washed with cold ethanol and then with water to give the ether **4** (1.90 g, 70%); recrystallization from ethanol afforded a pure analytical sam-

ple, m.p. 97−98 °C. − ^{1}H NMR (CDCl$_3$): δ = 6.6 (s, 2H, CH$_2$), 7.0−8.1 (m, 11H, aromatic H). − ^{13}C NMR (CDCl$_3$): δ = 74.5 (CH$_2$), 109.7, 109.8, 118.3, 119.9, 124.3, 124.5, 126.5, 127.0, 127.4, 128.0, 129.7, 129.8, 132.6, 133.9, 146.1, 153.8.

C$_{17}$H$_{13}$N$_3$O (275.3)   Calcd. C 74.17 H 4.76 N 15.26
                           Found C 73.96 H 4.74 N 15.32

Table 2. Atomic coordinates ($\times$ 10^4) and isotropic thermal parameters ($\times$ 10^3) [Å^2] for **4**

	x	y	z	U*
N(1)	−1206(2)	6100(3)	3279(1)	48(1)
N(2)	−2301(2)	6070(4)	3390(1)	61(1)
N(3)	−2897(2)	6142(4)	3062(1)	61(1)
C(4)	−2205(2)	6224(4)	2722(1)	48(1)
C(5)	−1119(2)	6195(4)	2861(1)	44(1)
C(6)	−210(2)	6271(4)	2599(1)	53(1)
C(7)	−452(3)	6336(4)	2186(1)	58(1)
C(8)	−1546(3)	6332(4)	2044(1)	61(1)
C(9)	−2432(3)	6280(4)	2304(1)	59(1)
C(10)	−361(3)	5924(4)	3588(1)	55(1)
O(11)	19(2)	7820(3)	3676(1)	64(1)
C(12)	980(2)	7961(4)	3905(1)	50(1)
C(13)	1434(3)	6505(4)	4129(1)	56(1)
C(14)	2467(3)	6761(4)	4337(1)	54(1)
C(15)	3005(3)	8561(5)	4311(1)	59(1)
C(16)	2478(3)	10041(5)	4084(1)	65(1)
C(17)	1500(3)	9767(5)	3894(1)	59(1)
C(18)	2967(3)	5311(6)	4566(1)	70(1)
C(19)	3974(3)	5572(6)	4754(1)	81(1)
C(20)	4523(3)	7329(7)	4716(1)	84(2)
C(21)	4052(3)	8783(5)	4503(1)	74(1)
N(1')	3362(2)	8782(3)	1804(1)	52(1)
N(2')	4451(2)	8621(4)	1691(1)	60(1)
N(3')	5042(2)	8488(4)	2020(1)	66(1)
C(4')	4350(2)	8574(4)	2358(1)	50(1)
C(5')	3265(2)	8758(4)	2218(1)	45(1)
C(6')	2355(2)	8902(4)	2486(1)	57(1)
C(7')	2600(3)	8855(4)	2893(1)	62(1)
C(8')	3701(3)	8674(4)	3043(1)	67(1)
C(9')	4580(3)	8535(5)	2782(1)	61(1)
C(10')	2527(2)	9070(4)	1494(1)	55(1)
O(11')	2044(2)	7258(3)	1409(1)	63(1)
C(12')	1086(2)	7280(4)	1171(1)	53(1)
C(13')	717(3)	8832(4)	962(1)	54(1)
C(14')	−301(2)	8739(4)	737(1)	55(1)
C(15')	−929(3)	7049(5)	742(1)	60(1)
C(16')	−496(3)	5460(4)	955(1)	65(1)
C(17')	496(3)	5551(5)	1162(1)	62(1)
C(18')	−725(3)	10329(5)	521(1)	65(1)
C(19')	−1718(3)	10220(7)	320(1)	77(1)
C(20')	−2334(3)	8547(6)	323(1)	81(2)
C(21')	−1965(3)	6974(6)	528(1)	74(1)

*) Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 1. Summary of crystal data and experimental details for compounds **4, 8,** and **9**

Compound	4	8	9
formula	C$_{17}$H$_{13}$N$_3$O	C$_{18}$H$_{15}$N$_2$O	C$_{19}$H$_{17}$N$_2$OI
molecular mass	275.31	283.33	416.26
space group	Pca2$_1$	I4$_1$/a	P2$_1$/c
a [Å]	12.022(2)	15.243(4)	7.772(2)
b [Å]	7.002(1)		22.435(7)
c [Å]	32.474(5)	24.781(6)	10.595(3)
β [°]			111.27(2)
V [Å^3]	2733.5(8)	5758(2)	1721.6(9)
Z	8	16	4
σ$_{calcd.}$ [g · cm^{-3}]	1.338	1.307	1.606
crystal size [mm]	0.03 × 0.19 × 0.19	0.27 × 0.17 × 0.17	0.03 × 0.12 × 0.24
radiation	Cu-K$_\alpha$	Cu-K$_\alpha$	Mo-K$_\alpha$
μ [cm^{-1}]	6.53	6.38	18.44
2Θ range [°]	3−110	3−110	3−50
scan speed [°/min]	2−29.3	2−29.3	2−29.3
orientation matrix			
number of reflections	22	22	23
2Θ range [°]	16−31	11−27	6−23
number of reflections measured	2101	2141	3455
number of unique reflections	1767	1876	3050
number of reflections $w/F > 3\sigma F$	1607	1635	2542
R	0.030	0.032	0.038
R$_w$	0.030	0.037	0.043
number of parameters	483	257	267
shift/esd	0.184	0.195	0.82
GOF	1/041	1.328	1.247
max, min in diff map	0.12, −0.13	0.10, −0.10	0.72, −1.21
g	0.0015	0.00072	0.00131

Table 3. Atomic coordinates ($\times$ 10^4) and isotropic thermal parameters ($\times$ 10^3) [Å^2] for **8**

	x	y	z	U*
N(1)	6495(1)	5278(1)	−1104(1)	60(1)
C(2)	6360(1)	6102(1)	−1296(1)	68(1)
N(3)	5948(1)	6123(1)	−1757(1)	75(1)
C(4)	5804(1)	5243(1)	−1882(1)	67(1)
C(5)	6147(1)	4711(1)	−1479(1)	58(1)
C(6)	6131(1)	3801(2)	−1499(1)	75(1)
C(7)	5752(2)	3438(2)	−1947(1)	79(1)
C(8)	5387(2)	3961(3)	−2351(1)	109(1)
C(9)	5403(1)	4863(2)	−2328(1)	92(1)
C(10)	6926(1)	5036(1)	−612(1)	62(1)
O(11)	6260(1)	4798(1)	−238(1)	65(1)
C(12)	6540(1)	4428(1)	239(1)	53(1)
C(13)	7394(1)	4314(1)	382(1)	52(1)
C(14)	7604(1)	3923(1)	885(1)	51(1)
C(15)	6923(1)	3655(1)	1235(1)	53(1)
C(16)	6046(1)	3789(1)	1067(1)	60(1)
C(17)	5855(1)	4165(1)	585(1)	60(1)
C(18)	8484(1)	3799(1)	1054(1)	62(1)
C(19)	8667(1)	3451(1)	1549(1)	69(1)
C(20)	7991(1)	3204(1)	1897(1)	69(1)
C(21)	7142(1)	3290(1)	1745(1)	62(1)
O(1)**	5000	7500	−2402(1)	111(1)

*) Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor. − **) Water molecule.

1-[(2-Naphthyloxy)methyl]-1H-benzimidazole Hemihydrate[20] **(8)**: Obtained from 1-(chloromethyl)-1H-benzimidazolium chloride (**7**; 2.03 g, 10 mmol) and sodium 2-naphthoxide (3.32 g, 20 mmol) by the procedure described for **4**; yield 1.64 g (60%); recrystalliza-

tion from ethanol afforded a pure analytical sample, m.p. 127−128°C. − ¹H NMR ([D₆]DMSO): 6.3 (s, 2H, CH₂), 6.9−7.9 (m, 11H, aromatic H), 8.4 (s, 1H, 2-H). − ¹³C NMR ([D₆]DMSO): 71.7 (CH₂), 109.5, 110.8, 118.7, 119.6, 122.4, 123.1, 123.2, 124.3, 126.6, 126.8, 127.6, 129.1, 129.7, 133.9, 143.5, 144.5, 153.7.

$C_{18}H_{14}N_2O \cdot 0.5 \, H_2O$ (283.2)　Calcd. C 76.31 H 5.34 N 9.89
　　　　　　　　　　　　　　　　Found C 76.39 H 5.43 N 9.83

1-Methyl-3-[(2-naphthyloxy)methyl]-1H-benzimidazolium Iodide **(9)**: Compound **8** (0.56 g, 2 mmol) and methyl iodide (0.30 ml, 5 mmol) were heated in ethanol (2.5 ml) to reflux for 6 h. After cooling, the precipitate was filtered and washed with ethanol to give the salt **9** (0.65 g, 80%); recrystallization from ethanol afforded a pure analytical sample, m.p. 177−178°C. − ¹H NMR ([D₆]DMSO): 4.1 (s, 3H, CH₃), 6.9 (s, 2H, CH₂), 7.3−8.4 (m, 11H, aromatic H), 10.2 (s, 1H, 2-H). − ¹³C NMR ([D₆]DMSO): 33.8 (CH₃), 73.7 (CH₂), 110.1, 113.8, 113.9, 118.3, 124.7, 126.7, 126.8, 126.9, 127.2, 127.5, 129.4, 129.9, 130.2, 131.8, 133.6, 143.3, 152.8.

$C_{19}H_{17}IN_2O$ (416.3)　Calcd. C 54.82 H 4.12 N 6.73
　　　　　　　　　　　　　Found C 54.94 H 4.11 N 6.68

Crystal Structure Analyses of **4**, **8** *and* **9**: The intensity data for **4** and **8** were measured using Ni-filtered Cu-K_α radiation, $\lambda = $ 1.54178 Å, and a P1 diffractometer upgraded to a P3. The data for **9** were measured using a Nicolet R3m diffractometer with graphite-monochromatized Mo-K_α radiation, $\lambda = 0.71069$ Å. In all three cases two standard reflections were measured after every 98 reflections and were used to correct for small variations in the standard

Table 4. Atomic coordinates (× 10⁴) and isotropic thermal parameters (× 10³) [Å²] for **9**

	x	y	z	U*
I	8967(1)	1270(1)	7053(1)	61(1)
N(1)	10346(4)	-753(2)	8426(3)	40(1)
C(2)	10325(6)	-1198(2)	9245(4)	44(2)
N(3)	9235(5)	-1629(2)	8536(4)	45(1)
C(4)	8513(6)	-1462(2)	7189(4)	44(1)
C(5)	9210(5)	-903(2)	7109(4)	43(2)
C(6)	8734(7)	-588(2)	5907(5)	54(2)
C(7)	7519(8)	-870(3)	4787(5)	71(2)
C(8)	6797(8)	-1436(3)	4859(6)	75(2)
C(9)	7277(6)	-1747(2)	6053(5)	57(2)
C(10)	11384(6)	-200(2)	8804(4)	43(2)
O(11)	12190(4)	-214(1)	10215(3)	50(1)
C(12)	13346(5)	253(2)	10796(4)	39(1)
C(13)	13639(5)	733(2)	10119(4)	42(1)
C(14)	14835(5)	1198(2)	10822(4)	41(1)
C(15)	15701(5)	1158(2)	12255(4)	41(1)
C(16)	15337(6)	652(2)	12913(4)	46(2)
C(17)	14210(5)	210(2)	12221(4)	45(2)
C(18)	15199(6)	1700(2)	10156(5)	51(2)
C(19)	16289(6)	2148(2)	10870(5)	54(2)
C(20)	17122(6)	2115(2)	12288(5)	58(2)
C(21)	16840(6)	1634(2)	12960(5)	50(2)
C(22)	8872(8)	-2194(2)	9108(6)	63(2)

*⁾ Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 5. Significant bond lengths [Å]ᵃ⁾ (entries in parantheses: most stable conformations)

	Compound 4				Compound 8				Compound 9			
ΔH_f (kcal/mol)	128.0	98.7	73.6		90.4	61.3	57.8		232.6	200.3	204.6	
	(123.6)	(96.3)	(70.6)		(87.1)	(60.5)	(55.6)		(229.1)	(197.2)	(201.7)	
Bond	X-Ray	AM1	PM3	MNDO	X-Ray	AM1	PM3	MNDO	X-Ray	AM1	PM3	MNDO
1-2	1.364(3)	1.369	1.396	1.355■	1.358(2)	1.418	1.419●	1.417●	1.326(6)	1.373	1.376●	1.373
2-3	1.284(4)	1.257	1.255	1.256	1.304(2)	1.336	1.330	1.328	1.325(6)	1.374	1.376	1.376●
3-4	1.385(4)	1.431	1.428●	1.417	1.395(3)	1.415	1.419	1.404	1.382(6)	1.417	1.423	1.419●
4-5	1.381(4)	1.449●	1.413	1.434●	1.388(3)	1.454●	1.416	1.437	1.381(8)	1.447■	1.415	1.432
5-1	1.356(4)	1.399	1.402	1.415	1.377(2)	1.406	1.425	1.411	1.394(5)	1.417	1.423	1.419
5-6	1.385(4)	1.397	1.399	1.414	1.388(3)	1.397	1.398	1.412	1.384(8)	1.400	1.401●	1.415
4-9	1.396(4)	1.399	1.402	1.415	1.389(3)	1.364	1.402	1.415	1.394(6)	1.399	1.402	1.415
6-7	1.373(5)	1.390	1.383	1.397	1.370(3)	1.389	1.383	1.398	1.374(8)	1.389	1.382	1.399
7-8	1.395(5)	1.406	1.408	1.426	1.395(5)	1.404	1.407	1.422	1.40(11)	1.406●	1.410	1.424
8-9	1.359(5)	1.390	1.384	1.397	1.376(5)	1.389	1.383	1.397■	1.372(9)	1.390●	1.382	1.399
1-10	1.434(4)	1.438	1.465	1.473	1.433(2)	1.423	1.459	1.463	1.455(6)	1.452	1.485	1.503
		(1.447)	(1.477)	(1.482)		(1.428)	(1.470)	(1.470)		(1.461)	(1.494)	(1.516)
10-11	1.433(4)	1.446	1.417	1.403	1.421(2)	1.449	1.417	1.405	1.396(5)	1.429	1.405	1.387
		(1.424)	(1.409)	(1.395)		(1.430)	(1.411)	(1.399)		(1.412)	(1.395)	(1.379)
11-12	1.379(4)	1.382	1.379	1.363	1.378(2)	1.380■	1.378■	1.363	1.372(5)	1.397	1.392	1.378
		(1.386)	(1.387)	(1.374)		(1.383)	(1.383)	(1.372)		(1.399)	(1.397)	(1.382)
12-13	1.367(4)	1.379	1.376	1.394	1.360(2)	1.379	1.376	1.394	1.357(7)	1.375	1.373	1.392
13-14	1.428(4)	1.422	1.421■	1.438	1.418(2)	1.422	1.421	1.439	1.416(6)	1.423	1.422	1.439
14-15	1.419(4)	1.418■	1.410	1.433	1.413(2)	1.418	1.409	1.433	1.423(6)	1.418	1.410	1.434
12-17	1.408(4)	1.422	1.422	1.441	1.410(2)	1.429	1.426	1.441	1.416(5)	1.425	1.422	1.440
3-22	-	-	-	-	-	-	-	-	1.477(8)	1.436	1.467	1.482■
										(1.436)	(1.466)	(1.482)
1ᵇ	-	0.020	0.020	0.027	-	0.023	0.019	0.027	-	0.025	0.021	0.027
1ₘₐₓᶜ	-	0.068	0.043	0.053	-	0.066	0.061	0.059	-	0.065	0.052	0.050
1ₘᵢₙᵈ	-	0.001	0.001	0.009	-	0.002	0.000	0.003	-	0.002	0.001	0.005

ᵃ⁾ Optimized with fixed dihedral angles 3−2−1−10, 2−1−10−11, 1−10−11−12, 10−11−12−13 (see Table 7, X-ray results). − ᵇ⁾ Average deviation from X-ray data. − ᶜ⁾ Referring to bond marked with ●. − ᵈ⁾ Referring to bond marked with ■.

Table 6. Significant bond angles [°][a] (entries in parantheses: most stable conformations)

Angle	Compound 4				Compound 8				Compound 9			
	X-Ray	AM1	PM3	MNDO	X-Ray	AM1	PM3	MNDO	X-Ray	AM1	PM3	MNDO
1-2-3	108.7	112.0	110.2	111.7	113.8	113.4■	109.9	112.6	109.2	110.6	108.4	110.1
2-3-4	109.0	109.5	110.3	109.3●	104.3	105.5	108.3	106.2	109.1	107.9	109.3	108.3
3-4-5	107.9	106.1	107.0	106.7	110.0	109.4	108.7	109.8■	106.6	106.8	106.5■	106.6■
4-5-6	122.9	121.3	121.5	121.5	123.5	121.3●	121.5	121.4	122.6	120.9●	121.2	121.1
5-6-7	115.7	116.9	116.6	116.4	116.4	117.3	116.9■	117.0	115.7	117.2	117.0	117.1
6-7-8	121.7	122.1	122.0	122.3	120.9	121.8	121.8	121.9	122.4	121.9	121.7	121.7
7-8-9	122.0	121.9■	121.8■	121.7●	122.5	121.8	121.8	121.6	121.8	122.0	121.9■	121.7
2-1-10	119.9	125.1●	123.8	121.2	127.3	126.4	125.6	125.8	126.5	126.4■	128.3	128.4
		(125.2)	(122.5)	(121.3)		(127.2)	(126.3)	(126.2)		(126.1)	(124.9)	(125.3)
1-10-11	106.2	107.7	101.6●	105.5	107.0	108.6	102.3●	106.2	105.3	106.4	103.2●	105.8
		(113.7)	(110.1)	(110.0)		(114.5)	(109.6)	(110.0)		(112.5)	(108.2)	(108.6)
10-11-12	116.1	114.6	117.0	123.8■	116.2	115.1	117.3	124.2●	115.5	114.7	116.9	124.0●
		(118.7)	(118.0)	(122.1)		(118.7)	(118.5)	(122.2)		(115.3)	(117.3)	(121.5)
11-12-13	124.7	125.0	125.6	125.8	124.9	125.5	125.9	126.1	125.1	124.8	125.6	125.5
12-13-14	120.2	119.5	119.3	120.5●	121.5	119.5	119.2	120.6	120.7	119.1	118.9	120.2
2-3-22	-	-	-	-	-	-	-	-	124.9	125.4	124.7	124.0
										(125.4)	(124.9)	(124.2)
1[b]	-	1.5	1.5	1.6	-	1.1	1.9	1.7	-	0.9	1.0	1.4
1max[c]	-	5.2	4.6	7.7	-	2.2	4.7	8.0	-	1.7	2.1	8.5
1min[d]	-	0.1	0.2	0.3	-	0.4	0.5	0.2	-	0.1	0.1	0.0

[a] See Table 5. — [b] Average deviation from X-ray data. — [c] Referring to bond angle with ●. — [d] Referring to bond angle with ■.

Table 7. Significant dihedral angles [°], most stable conformations

Dihedral Angle	Compound 4				Compound 8				Compound 9			
	X-Ray	AM1	PM3	MNDO	X-Ray	AM1	PM3	MNDO	X-Ray	AM1	PM3	MNDO
3-2-1-10	-176.6	173.4	164.9	178.9	180.8	178.9	179.1	-179.6	179.6	177.2	177.2	179.8
2-1-10-11	-98.7	-102.0	-92.3	-103.1	103.5	-109.9	-106.4	-104.2	-6.0	-100.2	-86.7	-108.0
1-10-11-12	-167.8	76.7	97.2	5.9	171.5	74.5	99.5	80.4	176.0	81.2	93.2	96.6
10-11-12-13	-16.0	11.3	17.5	72.7	3.0	11.1	-11.7	72.7	4.9	64.5	20.1	78.6
11-12-13-14	176.3	177.8	177.1	175.1	-179.9	177.5	-178.9	175.0	178.8	174.7	177.4	179.4
1-2-3-22	-	-	-	-	-	-	-	-	179.9	178.6	179.5	179.4

reflections. A summary of the crystal data and experimental details is given in Table 1. In all cases absorption corrections were made using ψ scans.

The three structures were each solved using direct methods and refined by blocked-cascade least-squares methods. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with $w = [\sigma^2(F) + g F_o^2]^{-1}$ where g is given in Table 1.

The scattering factors were the analytical form used in the SHELXTL package[21]. All calculations were performed using the SHELXTL package on a DG Model-30 Desktop Eclipse. The final atomic coordinates and isotropic thermal parameters are given in Tables 2, 3, and 4. Bond lengths, bond angles, and dihedral angles are summarized in Tables 5, 6, and 7. Views of the molecules together with the atomic numbering are given in Figures 1, 2, and 3. Additional X-ray data are available[22].

Semiempirical MO Calculations: All geometry optimizations were performed with the VAMP package (Erlanger Vectorized Molecular Orbital Package for CONVEX-C2 computers, version 4.0, which is based on AMPAC 1.0 and MOPAC 4.0) using the keyword "PRECISE". For further details see ref.[2b,c,11,12,15].

[1] See for example: [1a] A. R. Katritzky, S. Rachwal, K. C. Caster, F. Mahni, K. W. Law, O. Rubio, *J. Chem. Soc., Perkin Trans. 1,* 1987, 781; [1b] A. R. Katritzky, J.-J. Vanden Eynde, *J. Chem. Soc., Perkin Trans. 1,* submitted for publication.

[2] See for example: [2a] E. Anders, J. G. Tropsch, *Bull. Soc. Chim. Belg.* 96 (1987) 719; [2b] E. Anders, F. Markus, H. Meske, J. Tropsch, G. Maas, *Chem. Ber.* 120 (1987) 735; [2c] E. Anders, J. G. Tropsch, E. Irmer, G. M. Sheldrick, *Chem. Ber.* 123 (1990) 321.

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[11] The X-ray dihedral angle N1−C10−O11−C12 is 176.0° (Table 7), which is not that of the most stable conformation predicted by AM1. There is no possibility for the n(O)-σ*(N1−C10) overlap (anomeric effect). The AM1 method finds no compromise in optimizing the dihedral angles C2−N1−C10−O11 and N1−C10−O11−C12. The most stable conformers of **4**, **8**, and **9** [Tables 5 and 6 (values in parentheses) and 7] were determined by rotation about the N1−C10 and the C10−O11 bonds to give the (global) minimum as recently described by one of our research groups[2b,c]. These minima are completely optimized structures.

[12] The BLCF effect can be explained as follows using the pair of compounds **8** and **9** as examples. Methylation at N3 introduces a positive charge into the cyclically conjugated part of the molecule and thus decreases the σ-donor character of N1 in **9**. In terms of a "bond/no bond" resonance picture of the N1−C10 bonding, the importance of the "no bond" structure increases on alkylation. The localized orbital corresponding to the N1−C10 bond (calculated using the "LOCALIZE" keyword in the VAMP program) changes in character from a polar covalent bond in **8** (61.5% N1, 37.2% C10) towards a more localized nitrogen lone pair in **9** (64.7% N1, 34.0% C10). More significantly, the bond order N1−C10 drops from 0.914 in **8** to 0.845 in **9**. The heterocyclic moiety is therefore better suited as a leaving group in **9** than in **8**. Further work[13a,b] has shown that the BLCF effect is not limited to the pair of compounds considered here, but is a general effect.

[13] [13a] J. G. Tropsch, *Diplomarbeit*, Universität Erlangen-Nürnberg, 1987. − [13b] Further results (E. Anders, J. G. Tropsch, A. R. Katritzky) will be presented in a subsequent publication.

[14] For comparison: experimental (a) and AM1 calculated (b) N$^\oplus$−C(alkyl) bond lengths [Å]: *N*-methylpyridinium iodide: (a) 1.46(2), (b) 1.465; *N*-benzylpyridinium bromide: (a) 1.493(5), (b) 1.487. See ref.[2c].

[15] On suggestion of a referee, the reaction coordinates were recalculated with configuration interaction (CI). The RHF results shown in Figure 4 barely differ from the CI results (C.I. = 2 and PRECISE options in VAMP). The corresponding reaction curves run parallel to each other for these heteroaryl cations. CI gives a small (ca. 1 kcal/mol) stabilization that is essentially constant throughout the reaction, but requires far more CPU time. In cases other than the heterolytic bond fission considered here, the use of CI is often essential, especially for homolytic bond cleavages and for cases in which the HOMO-LUMO gap is very small at critical points on the reaction coordinate: See e.g. N. Kaila, R. W. Franck, J. J. Dannenberg, *J. Org. Chem.* **54** (1989) 4260.

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[22] Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-54326, the names of the authors, and the journal citation.

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