N,N-Coupled Heterobicycles from Cyclic Hydrazine Derivatives. Part 7.[1] Investigations on the Synthesis and Structure of 1-(N^1,N^2-Alkanediylcarbamimidoyl)pyrazolidine Derivatives

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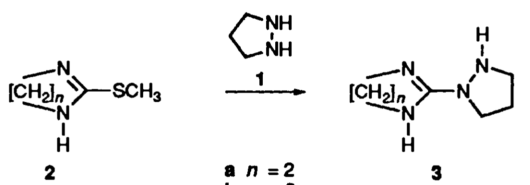
1-(N^1,N^2-Alkanediylcarbamimidoyl)pyrazolidines (containing either a dihydroimidazole or tetrahydrodiazepine ring unit) have been prepared in the form of crystalline iodine complexes from pyrazolidine and cyclic *N,N'*-alkanediyl-*S*-methylisothiouronium salts, and the structures were investigated by NMR spectroscopy, mass spectrometry and X-ray crystallography. The compounds exhibited resonance behaviour typical of monoprotonated aminoguanidine derivatives. In consequence of the resonance in the guanidine moiety, a planar area including members of both heterocyclic ring systems was formed in the molecule.

Many biologically active compounds are characterized by an aminoguanidine structure, which may be simply substituted or fused with various ring systems. In the search for drugs with heterocyclic aminoguanidine structures, compounds containing an aminoguanidine group shared by two different rings were designed for synthesis. Preparation of the 1-carbamimidoylpyrazolidines needed as starting compounds for the *N,N*-coupled heterobicycles was recently reported.[2] This work showed the reaction of pyrazolidine **1** with *S*-methylisothiouronium salts to be the preferred synthetic method. Proceeding from this, we describe here the preparation of 1-(N^1,N^2-alkanediylcarbamimidoyl)pyrazolidines **3** from **1** and cyclic *N,N'*-alkanediyl-*S*-methylisothiouronium salts **2**·HI (Scheme 1).[3-6]



a $n = 2$
b $n = 3$
c $n = 4$

Scheme 1

The structures of the compounds synthesised were examined by NMR spectroscopy, X-ray crystallography and mass spectrometry. An interesting structural question regarding these compounds is, does the same resonance phenomenon exist in them as in monoprotonated aminoguanidine?[7]

Results and Discussion

In accordance with expectation, the desired products **3a** and **3c** were formed by heating the respective starting compounds in ethanol for several hours. The products were isolated as crude hydroiodides in good yield. Because we used aqueous pyrazolidine, *N,N'*-alkanediylcarbamimidoylurea was formed as well. In the case of the **3b** hydroiodide the amount of the urea formed caused considerable difficulties in the purification of the target compound. Without a pure substance for elemental analysis, the elemental composition was determined by mass spectrometry. Under the same conditions, 2-methylsulfanylbenzimidazole did not react with **1** even with an extremely prolonged heating time, and the main product isolated was the free base.

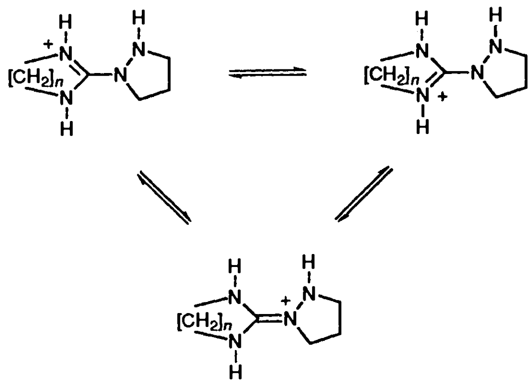
In connection with the crystallization of the **3a** hydroiodide we found that when treated with iodine it formed the complex **3a**·HI_3 (see the Experimental section). This compound existed as dark glittering crystals which were only sparingly soluble in water but slightly soluble in acetone. Analogously, other brown coloured **3**·HI_3 complexes were prepared starting from **3b** and **3c** hydroiodide.

^1H and ^{13}C spectra were recorded for all six compounds and the resonances are given in the Experimental section. The chemical shifts were assigned by the use of ^1H–^1H correlated COSY spectra. Assignments were easily made for the pyrazolidine ring of the HI salts, but for the HI_3 salts the NH–CH_2 signal was divided into two separate shifts with time, with no effect on the chemical shifts of the other CH_2 groups. This phenomenon may be explained in terms of the hindered nitrogen inversion in the pyrazolidine ring on the NMR time scale. The reaction took several months to go to completion.

The large NH–CH_2 coupling observed for HI salts indicates that the conformation of this group is not staggered, but rather that the NH proton is almost eclipsed with one of the protons of the CH_2 group, while forming an angle of *ca.* 160° with the other. However, for HI_3 salts the adjacent CH_2 group gives rise to only one multiplet, indicating that the NH proton is flipping fast from one side of the ring to the other (see X-ray, Fig. 1). The clearly different nature of these salts is further revealed by a comparison of the chemical shifts for the pyrazolidine ring NH protons, *ca.* 5.5 ppm in HI and *ca.* 3.4 ppm in HI_3 salts. The increased chemical shift for the HI compounds is due to the hydrogen bonding between nitrogens in adjacent rings. The hydrogen bonding is also seen in the X-ray results.

For all compounds, the other ring must contain a symmetry axis because only one $NHCH_2$ (**3a**) or $NHCH_2CH_2$ (**3b**, **3c**) fragment was observed. Moreover, the NH peak at the double bond region contained two equivalent protons, indicating that there is a hydrogen attached to both nitrogens. This is explained by the fast double bond resonance between the three guanidine nitrogens as presented in Scheme 2.

The results of X-ray crystal structure analyses of **3a**·HI_3 and **3c**·HI are in agreement with the results of the NMR measurements. The structures of the cations are shown in Fig. 1,



Scheme 2

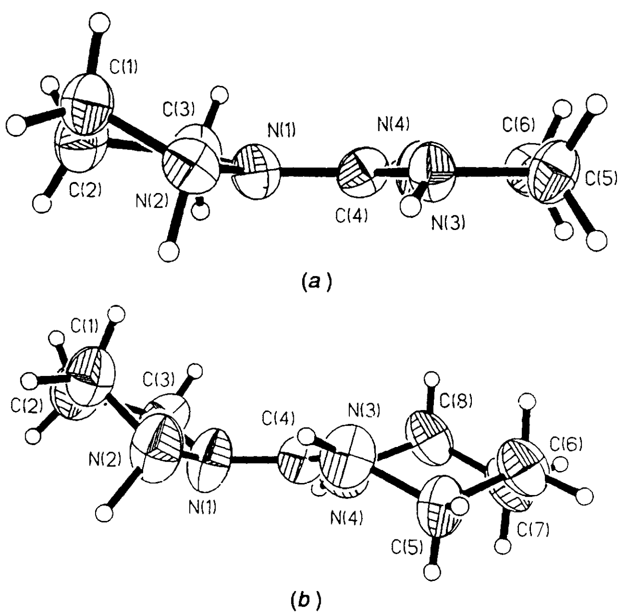


Fig. 1 Molecular structure of cations in compounds (*a*) **3a**·HI_3 and (*b*) **3c**·HI

and bond lengths and angles are given in Table 1. In both compounds, H atoms are attached to the N(3) and N(4) atoms, N(1)–C(4)–[N(3)]–N(4) moieties are planar, and the bond lengths in these moieties indicate a strong double bond character. In **3a**·HI_3 the bond lengths around the N(1) atom are significantly shorter and the bond angles larger relative to **3c**·HI. Moreover, the deviation of the N(1) atom out of the plane N(2)–C(3)–C(4) is 0.09 Å in **3a**·HI_3 but 0.27 Å in **3c**·HI, indicating slightly less sp^2 hybridization for N(1) in the latter structure. The intermolecular interaction between the N(2) and N(3) atoms is 2.79(1) and 2.65(1) Å in **3a**·HI_3 and **3c**·HI, respectively. In the **3c**·HI structure the position of the located H atom attached to N(3) also indicates the existence of an intramolecular hydrogen bond, which may explain the hindered nitrogen inversion in the pyrazolidine ring found in the NMR measurements. The pyrazolone ring is in a half-chair conformation in **3c**·HI, while an envelope conformation is found in **3a**·HI_3.

In the gas phase, after heating in the direct inlet probe, all the compounds studied most probably existed as free bases, as no peaks were observed in the mass spectra at larger mass numbers than the molecular ion peaks of the free bases. Despite the different ring sizes, the mass spectral behaviour of the 4,5-dihydroimidazole **3a**, 3,4,5,6-tetrahydropyrimidine **3b** and 4,5,6,7-tetrahydro-1*H*-1,3-diazepine **3c** derivatives was very similar. All compounds gave rise to a strong molecular ion peak. α-Cleavage reactions with respect to the nitrogen atoms dominated as is typical of nitrogen compounds. The ring systems in each compound were easily identified on the basis of these reactions because the connecting bond between the two rings was broken in spite of its double bond character. In addition to the *m*/*z* 71 ion from the pyrazolidine part of the molecules, this fragmentation gave rise to the *m*/*z* 69, 83 and 97 ions for compounds **3a**, **3b** and **3c**, respectively. It should be noted, however, that this bond cleavage also took place with hydrogen transfer to one or other of the ring systems. Another important fragmentation was the formal loss of C_2H_5 from the molecular ion, most probably taking place in two steps: namely, through loss of hydrogen atom followed by elimination of C_2H_4. Because the formation of the $[M - C_2H_5]^+$ ion was favourable for all the compounds studied, this fragmentation must have occurred in the pyrazolidine ring. However, since some elimination of CH_2=NH from compound **3a** took place as a consequence of α-cleavage with respect to the N(3) atom in the 4,5-dihydroimidazole ring, the elimination of C_2H_4 from compounds **3b** and **3c** probably partially took place from the larger ring.

Table 1 Bond lengths (Å) and angles (°) for $C_8H_{17}N_4^+$ in **3c**·HI and for $C_6H_{13}N_4^+$ in **3a**·HI_3

	3c·HI $C_8H_{17}N_4^+$	**3a**·HI_3 $C_6H_{13}N_4^+$
N(1)–N(2)	1.470(12)	1.419(11)
N(1)–C(3)	1.512(14)	1.456(11)
N(1)–C(4)	1.340(13)	1.309(12)
N(2)–C(1)	1.439(16)	1.473(13)
N(3)–C(4)	1.364(13)	1.350(11)
N(3)–C(5)	1.478(15)	1.483(13)
N(4)–C(4)	1.292(12)	1.332(13)
N(4)–C(8)	1.490(14)	1.465(14)[a]
C(1)–C(2)	1.481(17)	1.503(15)
C(2)–C(3)	1.503(15)	1.530(16)
C(5)–C(6)	1.504(14)	1.479(14)
C(6)–C(7)	1.518(13)	
C(7)–C(8)	1.508(17)	
N(2)–N(1)–C(3)	111.8(8)	114.2(7)
N(2)–N(1)–C(4)	117.5(9)	120.0(7)
C(3)–N(1)–C(4)	120.2(8)	124.5(8)
N(1)–N(2)–C(1)	101.9(8)	103.1(7)
C(4)–N(3)–C(5)	122.8(8)	110.6(8)
C(4)–N(4)–C(8)	125.2(9)	110.1(7)[b]
N(2)–C(1)–C(2)	108.1(10)	105.4(8)
C(1)–C(2)–C(3)	104.0(10)	104.1(9)
N(1)–C(3)–C(2)	101.3(8)	102.1(8)
N(1)–C(4)–N(3)	117.4(8)	124.7(9)
N(1)–C(4)–N(4)	120.0(9)	124.6(8)
N(3)–C(4)–N(4)	122.2(9)	110.7(8)
N(3)–C(5)–C(6)	117.1(9)	102.8(8)
C(5)–C(6)–C(7)	112.7(9)	105.8(9)[c]
C(6)–C(7)–C(8)	111.3(9)	
N(4)–C(8)–C(7)	115.9(9)	

[a] Bond length N(4)–C(6). [b] Bond angle C(4)–N(4)–C(6). [c] Bond angle C(5)–C(6)–N(4).

Experimental

The melting points were determined with a Kofler–Boetius apparatus and are uncorrected. The thin layer chromatography analysis was made on glass plates covered with Kieselgel G (Merck), where ethanol was used as the mobile phase and the Munier tetraiodobismuthate reagent[8] for detection. The UV spectra were measured on a SPECORD UV–VIS spectrophotometer (Carl Zeiss Jena), and the IR spectra on an FTIR 1600 (Perkin-Elmer). Elemental analyses were made with a 2400 CHN Elemental Analyser (Perkin-Elmer).

Table 2 Crystallographic data for $C_6H_{13}N_4^+ \cdot I_3^-$ (**3a**·HI_3) and $C_8H_{17}N_4^+ \cdot I^-$ (**3c**·HI)

	3a·HI_3	**3c**·HI
Crystal system	monoclinic	orthorhombic
Space group	$C2/c$	$P2_12_12_1$
a/Å	16.808(3)	7.056(2)
b/Å	8.800(2)	10.355(4)
c/Å	18.294(5)	16.351(5)
β/°	99.67(2)	
V/Å^3	2667.4(9)	1194.7(7)
Z	8	4
D_c/g cm^{-3}	2.599	1.647
Crystal dimensions (mm)	0.3 × 0.4 × 0.4	0.3 × 0.3 × 0.3
Radiation	Mo-Kα	Mo-Kα
μ/mm^{-1}	6.93	2.62
2θ limits (°)	5–55	4–55
Number of unique data	3071	1614
Number $F_{obs} > 6\sigma(F)$ (= M)	2176	990
Number of variables (= N)	118	118
$R\ [=\Sigma\lvert\Delta F\rvert/\Sigma\lvert F_o\rvert]$	0.053	0.034
$wR\ [=(\Sigma w\lvert\Delta F\rvert^2/\Sigma w\lvert F_o\rvert^2)^{\frac{1}{2}}]$	0.076	0.046
$g\ [w = \{\sigma^2(F) + gF^2\}^{-1}]$	0.004	0.001
$S\ [= \{(\Sigma w\lvert\Delta F\rvert^2)/(M-N)\}^{\frac{1}{2}}]$	1.062	1.093
Final $\Delta\rho_{max}/\Delta\rho_{min}$ (e$^-$ Å^{-3})	1.14/−1.96	0.649/−0.353

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM 400 WB spectrometer operating at 400.134 MHz for ^{1}H and 100.614 MHz for ^{13}C. For these measurements a sample of about 5 mg was added to 0.5 cm^3 [$^2H_6$]dimethyl sulfoxide with tetramethylsilane (TMS) as reference. The spectra were acquired using 32 kW data points with resolution enhancement and zero filling to point resolution better than 0.1 Hz. Decoupled ^{13}C spectra were measured using composite pulse sequence (Waltz decoupling). The proton chemical shifts were verified using the COSY technique. J values are given in Hz.

Details of crystal parameters, data collection parameters and refined data for compounds **3a**·HI_3 and **3c**·HI are summarized in Table 2. Intensity measurements were made on a Nicolet R3m diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å), ω-scan mode with a scan width of 1.2° for **3a**·HI_3 and 1.8° for **3c**·HI, and a variable scan speed of 2.02–29.3° min^{-1}. The data sets were corrected for Lorentz and polarization factors. Empirical absorption correction was made from Ψ-scan data for **3a**·HI_3. The transmission factors varied between 0.153 and 0.329.

The crystal structures were determined by direct methods and subsequent Fourier synthesis using the SHELXTL program package.[9] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at calculated positions with fixed isotropic thermal parameters (C–H = 0.96 Å and U = 0.07 Å^2 for **3a**·HI_3 and U = 0.08 Å^2 for **3c**·HI) except those attached to N atoms which were located from difference Fourier maps and not refined. The polarity of **3c**·HI was checked by inversion of all atomic parameters. The refinements converged to almost identical R values (R_1 = 0.034 and wR_1 = 0.046; R_2 = 0.036 and wR_2 = 0.048).

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.*

Mass spectra were measured with a Jeol JMS D300 mass spectrometer equipped with a combined EI/CI ion source and connected to a Jeol JMS 2000H data system. The EI operating conditions were as follows: electron energy 70 eV, ionization current 300 μA, source temperature 170 °C and acceleration voltage 3 kV. Samples were introduced through a direct inlet probe at temperatures 200–250 °C. Exact mass measurements were made at a resolution of 7000. In the case of low resolution mass spectra, only fragment ions with m/z values > 60 and relative intensities > 10% are presented below.

General Procedure for the Preparation of 1-(N^1,N^2-*Alkanediylcarbamimidoylpyrazolidines* **3**.—Pyrazolidine **1** (50% aqueous, 0.01 mol) was added to an ethanolic solution (10 cm^3) of the appropriate *N,N'*-alkanediyl-*S*-methylisothiouronium hydroiodide **2** (0.01 mol) and the mixture was refluxed for 6 h (14 h in the case of **3b** hydroiodide). All the solvent was removed and the residue was cooled after strong agitation with a glass rod. The crystals formed were suspended in a small amount of propanol, collected, recrystallized and dried *in vacuo*.

1-(4,5-*Dihydroimidazol*-2-*yl*)*pyrazolidine hydroiodide* **3a**·HI. The compound was obtained as colourless crystals (60%), m.p. 177–183 °C (from propanol); ν(KBr)/cm^{-1} 3169 (maximum of a broad peak; NH), 2981, 2880, 1663 (C=N), 1553 and 1288; δ_H 8.24 (2 H, br s), 5.59 (1 H, t, J 8.5), 3.63 (4 H, br s), 3.38 (2 H, t, J 7.2), 2.89 (2 H, m) and 2.09 (2 H, m); δ_C 159.30 (s), 46.92 (t), 46.86 (t), 42.98 (t) and 27.70 (t); m/z (EI, 70 eV) 140 (M$^{+\bullet}$, 73%), 139 (100), 138 (26), 137 (14), 112 (29), 111 (71), 110 (11), 98 (10), 82 (18), 71 (14), 70 (33), 69 (12) and 68 (12) (Found: C, 26.8; H, 4.6; N, 21.0%; M$^{+\bullet}$, 140.1053. Calc. for $C_6H_{13}IN_4$: C, 26.88; H, 4.89; N, 20.99%; $M^{+\bullet}$, 140.1062).

2-(*Pyrazolidin*-1-*yl*)-3,4,5,6-*tetrahydropyrimidine hydroiodide* **3b**·HI. The compound was obtained as colourless crystals (35%), m.p. 135–141 °C (from propanol); ν(KBr)/cm^{-1} 3348, 3246, 3182 (NH), 2966, 2943, 2881, 1633 (C=N), 1614, 1433 and 1316; δ_H 7.98 (2 H, br s), 5.26 (1 H, t, J 8.6), 3.35 (2 H, m), 3.30 (4 H, m), 2.84 (2 H, m), 2.11 (2 H, m) and 1.85 (2 H, m); δ_C 153.69 (s), 46.80 (t), 46.26 (t), 38.22 (t), 28.10 (t) and 19.50 (t); m/z (EI, 70 eV) 154 (M$^{+\bullet}$, 65%), 153 (42), 152 (24), 126 (29), 125 (100), 124 (27), 122 (10), 84 (58), 83 (30), 71 (15), 70 (19) and 69 (24) (Found: C, 31.1; H, 5.7; N, 20.55%; M$^{+\bullet}$, 154.1219. Calc. for $C_7H_{15}IN_4$: C, 29.80; H, 5.36; N, 19.86%; $M^{+\bullet}$, 154.1228).

2-(*Pyrazolidin*-1-*yl*)-4,5,6,7-*tetrahydro*-1H-1,3-*diazepine hydroiodide* **3c**·HI. The compound was obtained as colourless crystals (75%), m.p. 172–175 °C (from propanol); ν(KBr)/cm^{-1} 3186 (NH, maximum of a broad peak) 2941, 2920, 2870, 1611 and 1593; δ_H 7.76 (2 H, br s), 5.44 (1 H, t, J 8.4), 3.43 (2 H, t, J 7.6), 3.24 (4 H, m), 2.98 (2 H, m), 2.10 (2 H, m) and 1.63 (4 H m); δ_C 160.15 (s), 47.46 (t), 46.20 (t), 43.62 (t), 28.15 (t) and 26.94 (t); m/z (EI, 70 eV) 168 (M$^{+\bullet}$, 82%), 167 (52), 166 (20), 140 (30), 139 (100), 138 (25), 137 (17), 124 (13), 110 (12), 98 (62), 97 (52), 96 (10), 84 (15), 83 (14), 82 (20), 81 (12), 72 (37), 71 (23), 70 (59), 69 (25), 68 (24) and 64 (11) (Found: C, 32.3; H, 5.9; N, 19.0. Calc. for $C_8H_{17}IN_4$: C, 32.44; H, 5.79; N, 18.92%).

Preparation of Complex **3a**·HI_3.—*Method* 1. The propanolic mother liquor obtained from the preparation of **3a** hydroiodide was dried, after which acetone (2.5 cm^3) and aqueous iodine (1.5 mol dm^{-3}) containing hydroiodic acid were added to the residue. After 1 h the crystals that formed were collected, washed with water and a small amount of chloroform, and then dried. Further amounts of the product could be isolated by addition of water to the acetonic mother liquor; dark glittering crystals (22%), m.p. 139–143 °C; ν_{max}(CH_3OH)/nm 289 (log ε 3.62) and 363; ν(KBr)/cm^{-1} 3303, 3191 (NH), 2895, 1673 (C=N) and 1560; δ_H 8.25 (2 H, br s), 3.64 (4 H, br s), 3.41 (1 H, br s), 3.38 (2 H, m), 2.91 (2 H, t, J 6.4) and 2.10 (2 H, m); δ_C 159.29 (s), 46.97 (t), 46.87 (t), 42.95 (t) and 27.78 (t); m/z (EI, 70 eV) 140 (M$^{+\bullet}$, 74%) 139 (100), 138 (83), 137 (43), 112 (33), 11 (97), 110 (25), 98 (10), 96 (10), 84 (14), 83 (17), 82 (51), 81 (14), 71 (14), 70 (37), 69 (20), 68 (22) and 64 (10) (Found: C, 14.0; H, 2.4; N, 10.6. Calc. for $C_6H_{13}I_3N_4$: C, 13.81; H, 2.51; N, 10.74%).

Method 2. **3a** Hydroiodide (0.0001 mol) was dissolved in

* For details of the CCDC deposition scheme, see 'Instructions for Authors (1994)', *J. Chem. Soc., Perkin Trans. 2*, 1994, Issue 1.

hydroiodic acid (57%, 0.5 cm^3) and to this solution aqueous iodine (0.05 mol dm^{-3}, 3 cm^3) was added. The crystals, formed by slow crystallization, were collected, washed with water and a small amount of chloroform, and dried; yield 60%.

Preparation of Further Complexes **3**·HI_3.—**3b**·HI_3. Preparation was by method 2 (see **3a**·HI_3) starting from **3b** hydroiodide; dark brown crystals (90%), m.p. 107–108 °C; λ_{max}(CH_3OH)/nm 294 (log ε 3.57) and 366 (3.33); ν(KBr)/cm^{-1} 3314, 3196 (NH), 2949, 2877, 1640 and 1606; δ_H 8.00 (2 H, br s), 5.28 (1 H, br s), 3.32 (2 H, t, *J* 7.2), 3.28 (4 H, m), 2.82 (2 H, m), 2.07 (2 H, m) and 1.82 (2 H, m); δ_C 153.68 (s), 46.72 (t), 46.21 (t), 38.18 (t), 28.11 (t) and 19.48 (t); *m/z* (EI, 70 eV) 154 ($M^{+\bullet}$, 52%), 153 (35), 152 (31), 151 (12), 126 (25), 125 (100), 124 (34), 122 (14), 110 (11), 96 (10), 84 (52), 83 (28), 81 (10), 71 (13), 70 (23) and 69 (27) (Found: C, 16.3; H, 3.1; N, 10.4. Calc. for $C_7H_{15}I_3N_4$: C, 15.69; H, 2.82; N, 10.45%).

3c·HI_3. Preparation was by method 2 (see **3a**·HI_3) starting from **3c** hydroiodide; yellow–brown crystals (80%), m.p. 114–123 °C; λ_{max}(CH_3OH)/nm 289 (log ε 3.69) and 364 (3.85); ν(KBr)/cm^{-1} 3354, 3305, 3188 (NH), 2941, 1641 and 1574; δ_H 7.78 (2 H, br s), 3.40 (1 H, br s), 3.32 (2 H, m), 3.25 (4 H, m), 2.88 (2 H, t, *J* 6.5), 2.10 (2 H, m) and 1.63 (4 H, m); δ_C 160.20 (s), 47.40 (t), 46.20 (t), 43.65 (t), 28.17 (t) and 26.98 (t); *m/z* (EI, 70 eV) 168 ($M^{+\bullet}$, 59%), 167 (32), 166 (24), 140 (26), 139 (100), 138 (33), 137 (17), 124 (16), 111 (12), 110 (15), 108 (13), 98 (56), 97 (47), 96 (12), 84 (12), 83 (14), 82 (29), 81 (11), 72 (36), 71 (23), 70 (70), 69 (30), 68 (23) and 63 (10) (Found: C, 17.7; H, 3.0; N, 10.0%); $M^{+\bullet}$, 168.1373. Calc. for $C_8H_{17}I_3N_4$: C, 17.47; H, 3.12; N, 10.19%, $M^{+\bullet}$, 168.1374).

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