Diazepines, Part 28.[1] Crystal and Molecular Structures of some Dihydrodiazepinium Salts and Correlation with their Reactivity and Spectra

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The crystal and molecular structures of 6-bromo-5-methyl-7-phenyl-, 6-bromo-5,7-diphenyl- and 6-bromo-1,4-dimethyl-dihydrodiazepinium perchlorates have been determined. Some features of these structures, and of other recently determined structures of dihydrodiazepinium salts are discussed and compared with other properties, particularly the reactivity of 6-halogenodihydrodiazepinium salts towards nucleophiles, and the spectra and structure of 5,7-diphenyl derivatives.

The dihydrodiazepinium cation **1** includes a delocalised vinamidinium system[2] [N(4), C(5–7), N(1)] and in consequence, despite being a cation, undergoes electrophilic substitution reactions at C(6) which are similar to the electrophilic substitution reactions of benzene derivatives.[3] Rather surprisingly, many 6-halogenodihydrodiazepinium salts (**2**) react with nucleophiles, despite the apparent nucleophilic character of the C(6) site. Products may be either those obtained by direct nucleophilic substitution of the halogen atom or protodehalogenated products.[4] This reactivity has been rationalised in terms of the presence of a small amount of the tautomer **4**, which would be expected to be highly reactive towards nucleophiles. However, formation of **4** is disfavoured because the conjugation in structures **2** and **3**, estimated to be *ca.* 19 and 11 kcal mol^{-1}, respectively,[5] is thereby lost; indeed, any contribution from tautomer **4** must be very small since it has not been detected spectroscopically. There will, however, be some energetic compensation if R^1 and R^2 are large, because in the formation of **4**, C(6) becomes tetrahedral and this results in less crowding between the substituents R^1, Hal and R^2.

Since all 6-halogeno derivatives previously investigated had undergone nucleophilic attack readily, it came as a surprise when the reactions of salt **2** (R^1=R^2=H) were investigated[6] that such reactions did not take place with this compound. This was explained as follows. When R^1=R^2=H there is no steric crowding in structures **2** and **3**, and hence there is no energetic compensation in the formation of **4**. Consequently, the unreactivity towards nucleophiles is attributed to there being a vanishingly small contribution from tautomer **4**.

It seemed important therefore to seek some confirmation of these presumptions of crowding by obtaining X-ray structural data on a variety of these compounds. In addition to the 6-bromo-5-methyl-7-phenyl, 6-bromo-5,7-diphenyl and 6-bromo-1,4-dimethyl derivatives, whose crystal and molecular structures are reported in this paper, the structures of 6-bromo- and 6-bromo-5,7-dimethyl-dihydrodiazepinium salts have recently been determined,[7] and the structures of all these compounds are considered in this paper.

Chemical studies of dihydrodiazepinium salts suggest that their reactions may be influenced markedly by small changes in the geometry and conformation brought about by substituent atoms or groups,[3] and some discussion of 6-unsubstituted analogues is also incorporated.

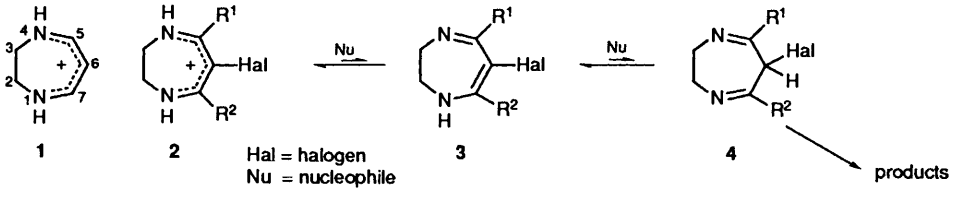
Experimental

Preparation of Dihydrodiazepinium Salts.—6-Bromo-5-methyl-7-phenyl and 6-bromo-5,7-diphenyl derivatives were prepared as described previously.[4] The 6-bromo-1,4-dimethyl derivative was prepared by adding bromine (0.16 g, 1 mmol) in methanol (3 cm^3) dropwise to a solution of 1,4-dimethyldihydrodiazepinium perchlorate (0.23 g, 1 mmol) in methanol (5 cm^3). Addition of diethyl ether completed precipitation of a product which was recrystallised from ethanolic perchloric acid to provide the perchlorate (0.18 g, 59%); m.p. 180–181 °C (from ethanol); λ_{max} 372 and 268 nm (ε 12 600 and 480); ν_{max}/cm^{-1} 1640, 1580, 1340, 1260, 1160, 1100 and 630; δ[$(CD_3)_2CO$] 3.59 (6 H, s), 4.00 (4 H, s) and 8.10 (2 H, s) (Found: C, 27.6; H, 4.05; N, 9.05. $C_7H_{12}BrClN_2O_4$ requires C, 27.7; H, 3.95; N, 9.25%).

Crystal Data.—6-Bromo-5-methyl-7-phenyl derivative. $C_{12}H_{14}BrClN_2O_4$, M = 365.6, monoclinic, a = 10.213(3), b = 13.216(3), c = 10.817(3) Å, β = 101.24(1)°, U = 1432(1) Å^3, Z = 4, D_c = 1.70 g cm^{-3}, μ(Mo-Kα) = 30.4 cm^{-1}, λ = 0.710 73 Å, F(000) = 736, space group $P2_1/c$ (uniquely from systematic absences).

6-Bromo-5,7-diphenyl derivative. $C_{17}H_{16}BrClN_2O_4$, M = 427.7, monoclinic, a = 9.051(1), b = 13.266(2), c = 15.062(3) Å, β = 99.38(1)°, U = 1784.3(9) Å^3, Z = 4, D_c = 1.59 g cm^{-3}, μ(Mo-Kα) = 24.5 cm^{-1}, λ = 0.710 73 Å, F(000) = 864, space group $P2_1/c$ (uniquely from systematic absences).

6-Bromo-1,4-dimethyl derivative. $C_7H_{12}BrClN_2O_4$. M = 303.6, triclinic, a = 8.244(2), b = 9.062(1), c = 8.051(1) Å, α = 104.54(1), β = 91.15(1), γ = 79.79(1)°, U = 572.8(3) Å^3, Z = 2, D_c = 1.76 g cm^{-3}, μ(Mo-Kα) = 37.8 cm^{-1}, λ = 0.710 73 Å, F(000) = 304, space group $P\bar{1}$.



1 **2** **3** **4**

Table 1 Crystallographic data

	Compound		
	6-Br, 5-Me, 7-Ph	6-Br, 5,7-Ph	6-Br-1,4-Me
Crystal dimensions/mm	0.32 × 0.35 × 0.46	0.17 × 0.33 × 0.43	0.13 × 0.27 × 0.35
$2\theta_{max}$ /°	52	58	60
Unique reflections	2803	4740	3324
Reflections with $I > 3\sigma(I)$	2041	2038	1807
Range of transmission coefficients	0.457–0.281	0.691–0.475	0.637–0.382
Number of variables	197	213	161
U_{iso} for H atoms/Å^2 Ph	0.065(6)	0.044(3)	—
Me	0.080(10)	—	0.075(7)
CH_2	0.043(5)	0.052(3)	0.058(8)
N–H	0.065(2)	0.032(3)	—
(sp^2) C–H	—	—	0.053(9)
R	0.0375	0.085	0.047
R_w	0.0448	0.095	0.052
p in weighting scheme	0.0008	0.0	0.0003
Residual density/e Å^{-3}	−0.60 to +0.77	−0.72 to +1.71	−0.71 to +0.82

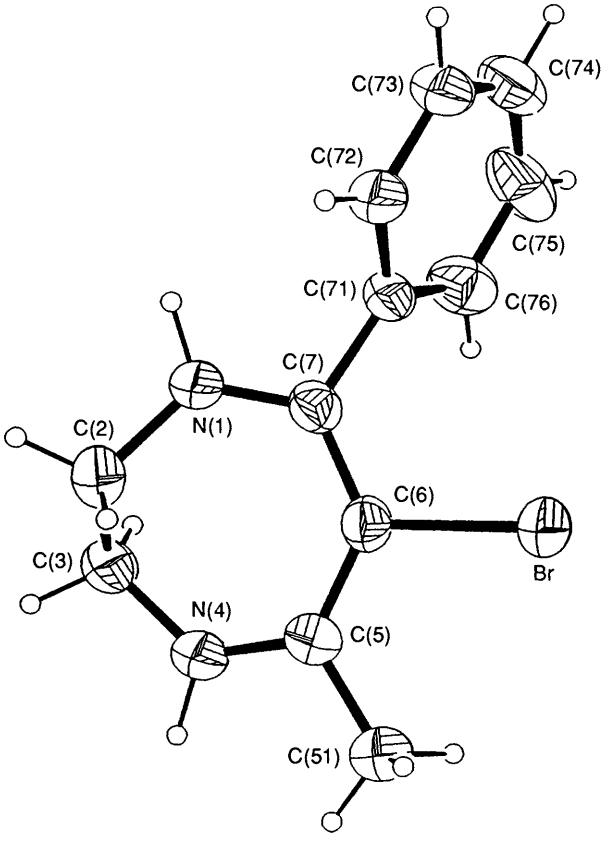


Fig. 1 Perspective view of the 6-bromo-5-methyl-7-phenyldihydrodiazepinium cation

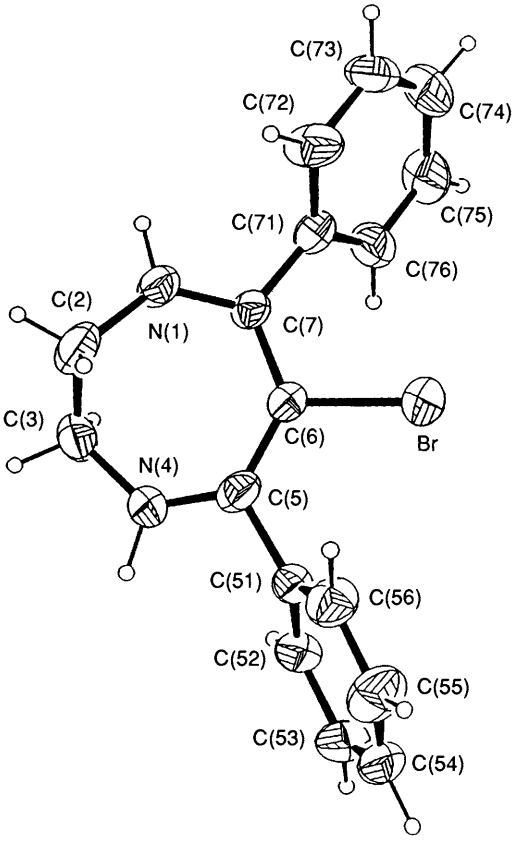


Fig. 2 Perspective view of the 6-bromo-5,7-diphenyldihydrodiazepinium cation

Data Collection, Structure Solution and Refinement.—All three compounds were treated in a similar manner; pertinent parameters for the data collection and refinement are collected in Table 1. Cell dimensions and crystal orientation matrices were determined by a least-squares refinement of 25 reflections with θ in the range 10–15°. Data were collected at 21 °C using a CAD4 diffractometer with graphite monochromated Mo-Kα radiation in the $\omega/2\theta$ scan mode; the ω scan width was $(0.70 + 0.35 \tan\theta)$°. Analysis of standard reflections monitored throughout the course of the data collections showed that there was no decay in the X-ray beam. Data were corrected for Lorentz, polarisation and absorption effects. The structures were solved by the heavy atom method and refined by full-matrix least-squares calculations. All non-hydrogen atoms were refined anisotropically except for the 5,7-diphenyl derivative where the oxygens of the perchlorate ion are disordered (these atoms were treated isotropically). Hydrogen atoms were visible in difference maps and were included as riding atoms with d(C–H) and d(N–H) 0.95 Å; individual U_{iso} values were refined for the various types of H atom (Table 1). Final difference maps were calculated after convergence was achieved (with all shift/error ratios <0.1) and were chemically featureless for the 5-methyl-7-phenyl and 1,4-dimethyl derivatives; there was some (expected) residual density adjacent to the disordered perchlorate oxygens in the 5,7-diphenyl derivative. Scattering factor data and anomalous dispersion corrections were taken

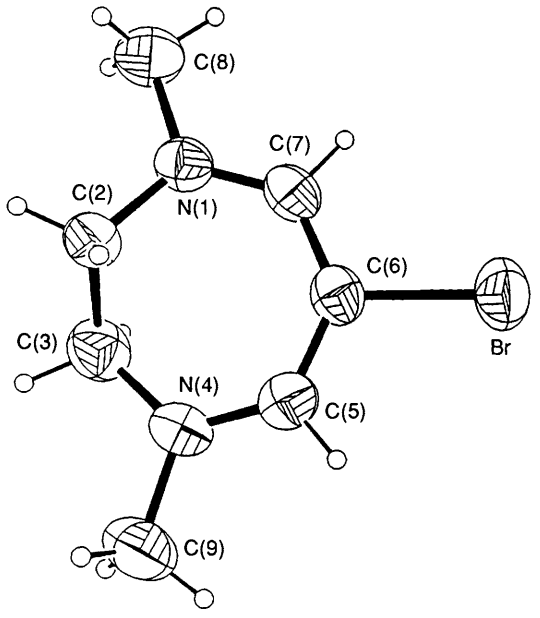


Fig. 3 Perspective view of the 6-bromo-1,4-dimethyldihydrodiazepinium cation

Table 2 Final fractional coordinates (Br and Cl × 10^5, others × 10^4) for 6-bromo-5-methyl-7-phenyldihydrodiazepinium perchlorate, $C_{12}H_{14}BrN_2^+ \cdot ClO_4^-$, with standard deviations in parentheses

Atom	*x*	*y*	*z*
Br	18 162(5)	15 593(3)	−78(3)
N(1)	2 643(4)	1 569(2)	3 814(3)
C(2)	2 986(4)	573(3)	4 331(3)
C(3)	1 797(4)	−131(3)	4 013(3)
N(4)	1 701(3)	−532(2)	2 776(3)
C(5)	1 799(4)	−31(3)	1 726(3)
C(6)	1 906(3)	1 032(3)	1 664(3)
C(7)	2 161(4)	1 770(3)	2 617(3)
C(51)	1 765(5)	−692(3)	608(4)
C(71)	1 927(4)	2 869(3)	2 368(3)
C(72)	2 955(5)	3 552(3)	2 794(4)
C(73)	2 736(5)	4 577(3)	2 635(4)
C(74)	1 498(5)	4 935(3)	2 092(4)
C(75)	479(5)	4 258(3)	1 648(5)
C(76)	694(5)	3 238(3)	1 783(4)
Cl	5 376(1)	25 297(7)	−37 529(9)
O(1)	752(6)	1 537(3)	−4 205(7)
O(2)	−858(3)	2 564(2)	−3 697(4)
O(3)	863(4)	3 225(3)	−4 638(4)
O(4)	1 375(6)	2 632(5)	−2 603(4)

Table 3 Final fractional coordinates (× 10^4) for 6-bromo-5,7-diphenyldihydrodiazepinium perchlorate, $C_{17}H_{16}BrN_2^+ \cdot ClO_4^-$, with standard deviations in parentheses

Atom	Occupancy factor (if not unity)	*x/a*	*y/b*	*z/c*
Br		1065(2)	1116(1)	1903(1)
Cl		3366(3)	5843(2)	2566(2)
N(1)		2754(9)	−512(5)	31(4)
C(2)		2292(12)	−1565(7)	265(6)
C(3)		4121(12)	−1708(7)	1098(6)
N(4)		3535(9)	−1494(5)	1909(5)
C(5)		2655(10)	−741(7)	2065(6)
C(51)		2255(10)	−758(6)	2994(5)
C(52)		3400(11)	−725(7)	3722(6)
C(53)		3057(12)	−810(7)	4596(6)
C(54)		1596(13)	−924(7)	4712(6)
C(55)		454(12)	−959(8)	3979(7)
C(56)		809(11)	−855(7)	3125(6)
C(6)		2231(10)	71(6)	1475(5)
C(7)		2446(10)	221(6)	561(5)
C(71)		2272(10)	1226(7)	133(5)
C(72)		1326(12)	1352(8)	−656(6)
C(73)		1159(13)	2285(8)	−1071(6)
C(74)		1929(13)	3083(8)	−691(7)
C(75)		2926(11)	2957(7)	102(7)
C(76)		3087(11)	2047(7)	514(7)
O(1)	0.94	4677(13)	6102(9)	2218(8)
O(2)	0.89	3776(13)	5247(9)	3353(8)
O(3)	0.61	2020(18)	6296(13)	2155(12)
O(4)	0.80	3024(19)	5150(15)	1946(13)
O(5)	0.76	3122(18)	6741(14)	3009(12)

Table 4 Final fractional coordinates for 6-bromo-1,4-dimethyldihydrodiazepinium perchlorate, $C_7H_{12}BrN_2^+ \cdot ClO_4^-$, (× 10^5 for Br, × 10^4 for others) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Br	8 096(7)	19 834(7)	24 736(6)
Cl	2 498(1)	6 856(1)	2 931(2)
O(1)	3 145(14)	5 543(7)	3 384(12)
O(2)	3 738(8)	7 712(8)	2 904(9)
O(3)	1 325(7)	7 733(9)	4 190(8)
O(4)	1 741(7)	6 504(8)	1 325(6)
N(1)	2 194(5)	2 449(4)	−2 135(5)
C(2)	2 514(6)	928(5)	−3 362(6)
C(3)	3 947(6)	−158(6)	−2 861(7)
N(4)	3 485(5)	−937(4)	−1 632(5)
C(5)	2 521(6)	−205(6)	−267(6)
C(6)	1 890(6)	1 369(6)	258(5)
C(7)	1 863(6)	2 566(5)	−517(6)
C(8)	2 172(8)	3 824(6)	−2 785(7)
C(9)	4 019(8)	−2 630(6)	−2 013(8)

Table 5 Selected bond lengths and angles in some dihydrodiazepinium cations

	Mean bond distance/Å			Mean bond angle/°	
Substituents	C(5 or 7)–C(6)	C(5 or 7)–N	C(6)–Br	N–C(5 or 7)–C(Me or Ph	C(6)–C(5 or 7)–C(Me or Ph)
Unsubstituted[10]	1.382(5)	1.306(9)	—	—	—
5,7-Me[11]	1.391(5)	1.318(5)	—	116.0(4)	118.4(4)
5,7-Ph[13]	1.395(6)	1.332(5)	—	115.6(4)	118.7(4)
6-Br[7]	1.390(8)	1.304(7)	1.904(5)	—	—
6-Br-5,7-Me[7]	1.413(6)	1.306(8)	1.918(3)	113.8(4)	121.6(3)
6-Br-5,7-Ph	1.423(12)	1.320(11)	1.916(8)	114.1(7)	121.3(8)
6-Br-5-Me-7-Ph:C(7)	1.407(5)	1.319(5)	1.924(3)	113.0(3)	123.0(3)
6-Br-5-Me-7-Ph:C(5)	1.411(5)	1.335(5)		114.0(3)	122.4(3)
6-Br-1,4-Me	1.383(7)	1.318(6)	1.917(4)	—	—

from ref. 8. The weighting scheme used in the refinements was of the form $w = 1/[\sigma^2 F_0 + p(F_0^2)]$. All calculations were performed with SHELX76.[9] Perspective views of the cations are given in Figs. 1–3.

Final refined atom coordinates for the three structures are given in Tables 2–4.. Principal dimensions are summarised in Table 5, and bond lengths and bond angles are given in Tables 6–8. Tables of calculated hydrogen atom coordinates and

Table 6 Bond lengths and angles for 6-bromo-5-methyl-7-phenyldihydrodiazepinium perchlorate

Bond lengths/Å	
Br–C(6)	1.924(3)
N(1)–C(2)	1.447(4)
N(1)–C(7)	1.319(5)
C(2)–C(3)	1.515(5)
C(3)–N(4)	1.424(5)
N(4)–C(5)	1.335(5)
C(5)–C(6)	1.411(5)
C(5)–C(51)	1.487(5)
C(6)–C(7)	1.407(5)
C(7)–C(71)	1.488(5)
C(71)–C(72)	1.393(5)
C(71)–C(76)	1.383(6)
C(72)–C(73)	1.378(6)
C(73)–C(74)	1.370(7)
C(74)–C(75)	1.386(7)
C(75)–C(76)	1.370(6)
Cl–O(1)	1.432(4)
Cl–O(2)	1.440(3)
Cl–O(3)	1.413(3)
Cl–O(4)	1.372(4)
Bond angles/°	
C(2)–N(1)–C(7)	125.4(3)
N(1)–C(2)–C(3)	110.3(3)
C(2)–C(3)–N(4)	110.3(3)
C(3)–N(4)–C(5)	127.7(3)
N(4)–C(5)–C(6)	123.6(3)
N(4)–C(5)–C(51)	114.0(3)
C(6)–C(5)–C(51)	122.4(3)
Br–C(6)–C(5)	114.6(3)
Br–C(6)–C(7)	113.9(2)
C(5)–C(6)–C(7)	131.4(3)
N(1)–C(7)–C(6)	124.0(3)
N(1)–C(7)–C(71)	113.0(3)
C(6)–C(7)–C(71)	123.0(3)
C(7)–C(71)–C(72)	119.2(3)
C(7)–C(71)–C(76)	121.8(3)
C(72)–C(71)–C(76)	118.9(3)
C(71)–C(72)–C(73)	120.1(4)
C(72)–C(73)–C(74)	120.4(4)
C(73)–C(74)–C(75)	119.6(4)
C(74)–C(75)–C(76)	120.3(5)
C(71)–C(76)–C(75)	120.6(4)
O(1)–Cl–O(2)	105.2(3)
O(1)–Cl–O(3)	107.1(3)
O(1)–Cl–O(4)	106.8(4)
O(2)–Cl–O(3)	111.9(2)
O(2)–Cl–O(4)	114.0(3)
O(3)–Cl–O(4)	111.3(3)
Hydrogen bond dimensions/Å	
N(1)···O(2)[a]	3.049(4)
N(1)–H(1)	0.95
N(4)···O(2)[b]	3.046(4)
N(4)–H(4)	0.95
O(2)[b]···H(4)	2.25
O(2)[a]···H1	2.31
N(1)–H(1)···O(2)[a]	135
N(4)–H(4)···O(2)[b]	141

[a] $0.5 + x, 0.5 - y, 1 + z$. [b] $-x, -y, -z$.

anisotropic thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC).*

Discussion

As found previously for the unsubstituted cation **1** [10] and its 5,7-dimethyl derivative,[11] the bond lengths of the vinamidinium systems are consistent with full delocalisation of the π-electrons in the system; this portion of the ring is helical and its ends are

* For details of the CCDC deposition scheme, see 'Instructions for Authors (1991)', *J. Chem. Soc., Perkin Trans. 2*, Issue 1.

Table 7 Bond lengths and bond angles for 6-bromo-5,7-diphenyldihydrodiazepinium perchlorate

Bond lengths/Å	
N(1)–C(2)	1.442(12)
N(1)–C(7)	1.317(10)
C(2)–C(3)	1.527(13)
C(3)–N(4)	1.438(11)
N(4)–C(5)	1.322(11)
C(5)–C(6)	1.410(12)
C(5)–C(51)	1.501(10)
C(51)–C(52)	1.381(12)
C(51)–C(56)	1.361(12)
C(52)–C(53)	1.405(12)
C(53)–C(54)	1.370(14)
C(54)–C(55)	1.384(14)
C(55)–C(56)	1.382(12)
C(6)–Br	1.916(8)
C(6)–C(7)	1.435(10)
C(7)–C(71)	1.478(12)
C(71)–C(72)	1.357(12)
C(71)–C(76)	1.387(13)
C(72)–C(73)	1.383(13)
C(73)–C(74)	1.343(14)
C(74)–C(75)	1.385(14)
C(75)–C(76)	1.355(13)
Cl–O(1)	1.416(12)
Cl–O(2)	1.422(12)
Cl–O(3)	1.409(16)
Cl–O(4)	1.311(20)
Cl–O(5)	1.400(19)
Bond angles/°	
C(2)–N(1)–C(7)	126.3(7)
N(1)–C(2)–C(3)	110.9(8)
C(2)–C(3)–N(4)	111.4(8)
C(3)–N(4)–C(5)	128.0(7)
N(4)–C(5)–C(6)	125.2(8)
N(4)–C(5)–C(51)	113.4(7)
C(6)–C(5)–C(51)	121.1(8)
C(5)–C(51)–C(52)	118.4(8)
C(5)–C(51)–C(56)	121.4(8)
C(51)–C(52)–C(53)	119.3(9)
C(52)–C(53)–C(54)	119.6(9)
C(53)–C(54)–C(55)	120.8(9)
C(54)–C(55)–C(56)	118.8(9)
C(55)–C(56)–C(51)	121.3(9)
C(5)–C(6)–C(7)	130.1(8)
C(5)–C(6)–Br	116.7(6)
C(7)–C(6)–Br	113.0(6)
C(6)–C(7)–N(1)	123.8(7)
C(6)–C(7)–C(71)	121.4(7)
N(1)–C(7)–C(71)	114.8(7)
C(7)–C(71)–C(72)	120.0(8)
C(7)–C(71)–C(76)	121.1(8)
C(71)–C(72)–C(73)	120.8(9)
C(72)–C(73)–C(74)	120.2(9)
C(73)–C(74)–C(75)	119.5(9)
C(74)–C(75)–C(76)	120.6(9)
C(75)–C(76)–C(71)	120.1(9)
O(1)–Cl–O(2)	108.9(7)
O(1)–Cl–O(3)	116.8(8)
O(1)–Cl–O(4)	91.2(9)
O(1)–Cl–O(5)	100.2(9)
O(2)–Cl–O(3)	133.9(9)
O(2)–Cl–O(4)	101.7(10)
O(2)–Cl–O(5)	96.7(9)
O(3)–Cl–O(4)	84.2(11)
O(3)–Cl–O(5)	69.7(9)
O(4)–Cl–O(5)	153.9(11)
Hydrogen bond dimensions/Å	
N(1)···O(2)[a]	2.851(14)
N(1)–H(1)	0.95
N(4)···O(5)[b]	2.927(19)
N(4)–H(4)	0.95
O(2)[a]···H(1)	1.94
O(5)[b]···H(4)	2.11
N(1)–H(1)···O(2)[a]	159
N(4)–H(4)···O(5)[b]	143

[a] $x, 0.5 - y, -0.5 + z$. [b] $x, -1 + y, z$.

Table 8 Bond lengths and bond angles for 6-bromo-1,4-dimethyldihydrodiazepinium perchlorate

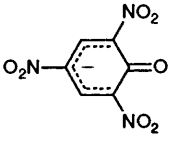
Bond lengths/Å	
Br–C(6)	1.917(4)
N(1)–C(2)	1.464(6)
N(1)–C(7)	1.310(6)
N(1)–C(8)	1.465(6)
C(2)–C(3)	1.515(7)
C(3)–N(4)	1.444(6)
N(4)–C(5)	1.327(6)
N(4)–C(9)	1.473(6)
C(5)–C(6)	1.388(7)
C(6)–C(7)	1.378(7)
Cl–O(1)	1.349(6)
Cl–O(2)	1.393(5)
Cl–O(3)	1.399(5)
Cl–O(4)	1.412(5)
Bond angles/°	
C(2)–N(1)–C(7)	120.3(4)
C(2)–N(1)–C(8)	118.2(4)
C(7)–N(1)–C(8)	121.4(4)
N(1)–C(2)–C(3)	112.6(4)
C(2)–C(3)–N(4)	113.1(4)
C(3)–N(4)–C(5)	122.5(4)
C(3)–N(4)–C(9)	117.3(4)
C(5)–N(4)–C(9)	120.0(4)
N(4)–C(5)–C(6)	127.3(4)
C(5)–C(6)–C(7)	132.5(4)
C(5)–C(6)–Br	113.6(3)
C(7)–C(6)–Br	113.9(3)
C(6)–C(7)–N(1)	127.0(4)
O(1)–Cl–O(2)	109.1(6)
O(1)–Cl–O(3)	108.1(6)
O(1)–Cl–O(4)	110.3(5)
O(2)–Cl–O(3)	107.9(4)
O(2)–Cl–O(4)	111.6(4)
O(3)–Cl–O(4)	109.7(4)

connected by a staggered dimethylene bridge. All the C–Br bond distances are similar. They are marginally greater than the mean C_{aryl}–Br distance (1.899),[12] and are in accord with a Br atom attached to a delocalised system. Distortion of the vinamidinium moiety due to crowding between vicinal substituents could involve either bond-lengthening or distortion of the bond angles, and both are evident in the 5,7-substituted 6-bromo-compounds. The mean C–C bond lengths of the vinamidinium systems are just significantly, but consistently, longer than the corresponding lengths in dihydrodiazepinium salts which do not have substituents at all three of the C(5–7) positions (Table 5).

Intramolecular crowding also affects the bond angles at the C(5,7) positions when a 6-bromo substituent is present. When the C(6) position is unsubstituted the N–C(5 or 7) –C(51 or 71) angles are similar to the C(6)–C(5 or 7) –C(51 or 71) angles, but when all three sites are occupied by substituents the C(6)–C(5 or 7)–C(51 or 71) are noticeably larger than the N–C–C angles. In the 6-bromo-5,7-dimethyl derivative the methyl groups are also displaced from the plane of the vinamidinium system by −0.367(6) and +0.357(6) Å, respectively, but the bromine atom is only 0.076(4) Å out of this plane; in the absence of the methyl groups the bromine atom is similarly −0.082(2) Å out of the plane. Thus, the molecular crowding which has been invoked to explain the differences in reactivity between 6-halogeno-5,7-unsubstituted and 6-halogeno-5,7-substituted dihydrodiazepinium salts appears to have a foundation in the perceived structures of these compounds.

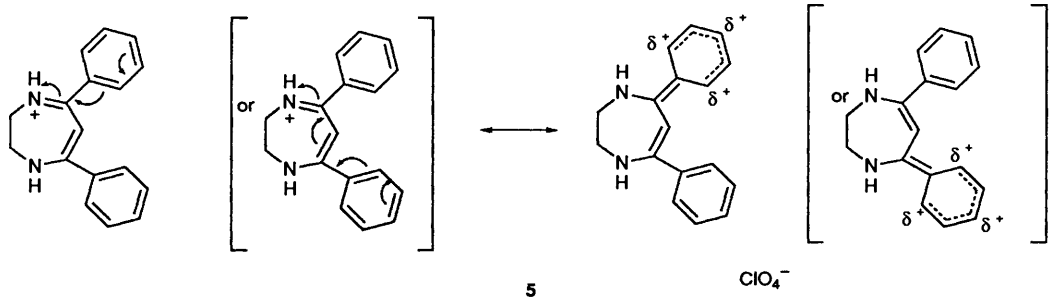
A 6-bromo substituent also forces vicinal phenyl groups to be twisted further out of the plane of the vinamidinium system. In 5,7-diphenyldihydrodiazepinium perchlorate (**5**)[13] the angles between the planes of the rings are 46.1(6) and 38.2(6)°. This value is very similar to that observed for biphenyl, either in solution [32(2)°][14] or in the gase phase [45(10)°];[15] the crystal forces which make biphenyl planar in its crystalline form will be less in the case of the dihydrodiazepinium salt since the seven-membered ring of the latter is not intrinsically planar. Introduction of a 6-bromo substituent results in increases in the angles between the planes to 59.4(7) and 68.1(7)°. Similarly in the 6-bromo-5-methyl-7-phenyl derivative the angle between the planes of the rings is 61.3(5)°.

The mean C–N distances of the vinamidinium system of **5** are appreciably longer [1.332(6) Å] than in the unsubstituted cation [1.306(9) Å]. 'Curved-arrow' analysis of **5** suggests that there is a donation of electrons into a dihydrodiazepinium ring from the phenyl groups located at the C(5 or 7) positions; this is confirmed by NMR spectroscopic evidence.[16] Contributions from these forms should result in a lengthening of the N(4)–C(5) and N(1)–C(7) bonds, although other steric factors such as *ortho–ortho* hydrogen interactions may also be involved. It may also be significant that the *ipso–ortho* bonds of the phenyl groups are longer [mean 1.397(7) Å] than the other bonds of these rings [mean 1.375(7) Å], in accord with electronic interaction with the vinamidinium system and concomitant setting up of pentadienium systems in the phenyl rings, as indicated. This type of structure mirrors the pentadienide structure (**6**) which we have found best represents the picrate anion as it exists in dihydrodiazepinium picrates.[7,10,17]



6

When the substituent phenyl groups are forced further out of plane with the seven-membered ring, because of the presence of a 6-bromo substituent, the lengths of the *ipso–ortho* bonds more closely resemble those of the remaining ring bonds [for 6-bromo-5-methyl-7-phenyl derivative: mean distances, respectively, 1.388(6) and 1.376(7) Å] and the interannular bond is marginally longer [1.488(5) Å], reflecting reduced electronic interaction between the rings. The present crystallographic results thus also support the suppositions, based on spectroscopic evidence, of



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electronic interaction into the vinamidinium system from 5,7-phenyl substituents, and that this may be diminished by the presence of an extra substituent at C(6).

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Paper 1/01183I
Received 13*th March* 1991
Accepted 18*th June* 1991