Nitrogen-14 and Chlorine-35 Quadrupole Resonance in Some *N*-(1-Chloro-2,4-diazabut-3-enylidene)-*N*,*N*-dimethylammonium Salts

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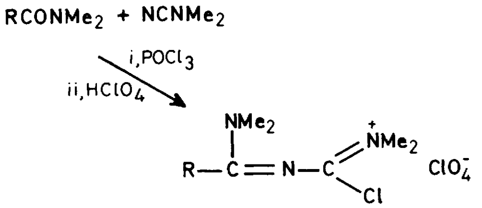
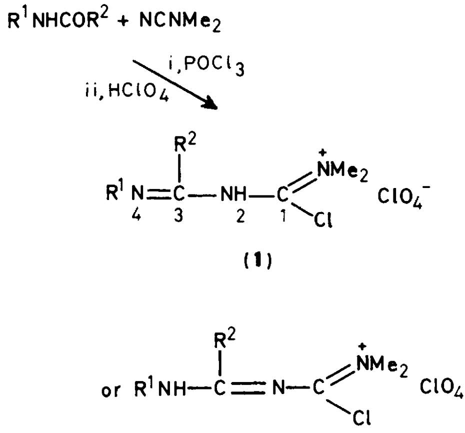
Nitrogen-14 and chlorine-35 quadrupole resonance frequencies have been measured at room temperature for a series of six closely related *N*-(1-chloro-2,4-diazabut-3-enylidene)-*N*,*N*-dimethylammonium salts and two related compounds. Reasonable assignments of all ^{14}N frequencies have been made and their variations with structure are discussed. The results support the structure $R^1N=CR^2-NH-CCl=\overset{+}{N}Me_2X-$ for all the salts examined; it appears to be the predominant resonance form, and the cation has therefore been named on this basis.

The synthesis of 1-chloro-1,3-bis(dimethylamino)-2-azapropenylium perchlorates from tertiary amides and dimethylcyanamide has recently been reported[1] [equation (1)]. In this paper, it is shown that this reaction can be extended to secondary amides to yield perchlorates of the *N*-(1-chloro-2,4-diazabut-3-enylidene)-*N*,*N*-dimethylammonium cation [equation (2)], the structure of which can be written in two tautomeric forms (**1**) and (**2**). This paper discusses a ^{14}N quadrupole double-resonance study of a number of salts of this cation to discover which tautomeric structure is adopted in the solid state. Chlorine-35 quadrupole resonance spectra are also reported; the results of both studies are related to the electronic structure of the cation and the influence of differing substituents and anions.



(1)

(R=Me, Ar, or ArCH$_2$)



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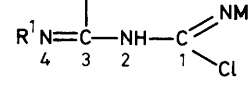
(**2**)



(**1**)

a; R^1 = Ph, R^2 = Me, X = ClO_4
b; R^1 = *p*-ClC_6H_4, R^2 = Me, X = ClO_4
c; R^1 = *p*-MeC_6H_4, R^2 = Ph, X = ClO_4
d; R^1 = Me, R^2 = Ph, X = ClO_4
e; R^1 = *p*-$EtOC_6H_4$, R^2 = Me, X = BF_4
f; R^1 = Bu^s, R^2 = Ph, X = Cl

Experimental

The salts were prepared by treating an equimolar mixture of the amide and dimethylcyanamide dissolved in dichloromethane with 1.3 mol equiv. of phosphoryl chloride below 10 °C. When i.r. spectra indicated that all the cyanamide had been consumed, the mixture was added to ice-cold aqueous perchloric acid, the organic phase was separated and evaporated under reduced pressure, and the residual gum was triturated with ethyl acetate.

(i) Acetanilide (12.15 g) gave (after 39 h) *N*-(1-chloro-3-methyl-4-phenyl-2,4-diazabut-3-enylidene)-*N*,*N*-dimethylammonium perchlorate (**1a**) (16.38 g, 65.2%), m.p. 112—112.5 °C (from acetone–ethyl acetate).

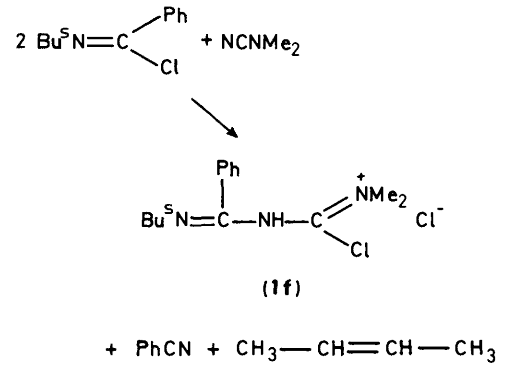
(ii) *p*-Chloroacetanilide (10.18 g) gave (after 138 h) *N*-(1-chloro-4-*p*-chlorophenyl-3-methyl-2,4-diazabut-3-enylidene)-*N*,*N*-dimethylammonium perchlorate (**1b**) (11.1 g, 50%), m.p. 146—147 °C (from acetone–ethyl acetate).

(iii) *N*-Benzoyl-*p*-toluidine (12.11 g) gave (after 168 h) *N*-(1-chloro-3-phenyl-4-*p*-tolyl-2,4-diazabut-3-enylidene)-*N*,*N*-dimethylammonium perchlorate (**1c**) (15.01 g, 64.4%), m.p. 201—202 °C (from acetonitrile–ethyl acetate).

(iv) *N*-Methylbenzamide (13.5 g) gave (after 23 h) *N*-(1-chloro-4-methyl-3-phenyl-2,4-diazabut-3-enylidene)-*N*,*N*-dimethylammonium perchlorate (**1d**) (24.84 g, 76.7%), m.p. 194—196 °C (from acetonitrile–ethyl acetate).

(v) Phenacetin (10.74 g) gave (after 27 h, and pouring into ice-cold aqueous tetrafluoroboric acid) *N*-(1-chloro-4-*p*-ethoxyphenyl-3-methyl-2,4-diazabut-3-enylidene)-*N*,*N*-dimethylammonium tetrafluoroborate (**1e**), 9.48 g (44.5%), m.p. 133.5—134.5 °C (from aqueous acetone).

(vi) *N*-(1-Chloro-3-phenyl-4-s-butyl-2,4-diazabut-3-enylidene)-*N*,*N*-dimethylammonium chloride (**1f**) was prepared as follows. A mixture of *N*-s-butylbenzamide (20.0 g), thionyl chloride (22 ml), and benzene (25 ml) was heated under reflux for 50 min. The resulting solution was filtered and evaporated under reduced pressure. The residual imidoyl chloride [see equation (3)] was heated with dimethylcyanamide (1 mol equiv.) on an oil-bath until a vigorous reaction set in at 138 °C (bath temp.). The bath was removed and the reaction was



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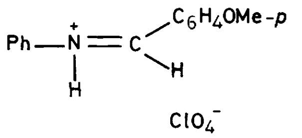

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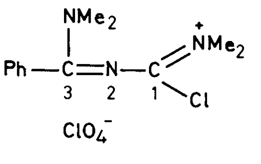


(4)

allowed to proceed. On cooling, a solid was formed. Ethyl acetate (35 ml) was added and the product was collected (16.5 g, 96.7%), m.p. 152—153 °C (from acetone).

The ^{14}N quadrupole double-resonance spectra of two other salts (**3**) and (**4**), and ^{35}Cl spectra of the latter, were also studied for comparison; the preparation of the latter has already been described.[1] Compound (**3**) was prepared by treating a solution of *N-p*-methoxybenzylideneaniline in chloroform with a slight excess of 70% perchloric acid, whereupon the salt separated (m.p. 246 °C). Microanalytical data for the compounds are given in Table 1 and some characteristic i.r. wavenumbers in Table 2. The ^{14}N quadrupole resonance spectra were recorded at room temperature (295 K) with a previously described sample-transfer spectrometer,[2,3] by means of level-crossing[4] and cross-relaxation[5] methods. The ^{35}Cl quadrupole resonance spectra were recorded with a Decca super-regenerative-oscillator spectrometer[6] at fixed temperatures of 77, 195, and 295 K.

Results and Discussion

All three ^{14}N signals (ν_x, ν_y, ν_z)[7] from nitrogen atoms directly attached to hydrogen or hydrogen-bonded are readily identified in level-crossing spectra, whereas other types (at least, at room temperature) tend to give only weak responses.[8] The ^{14}N frequencies for the NH group from both level-crossing and cross-relaxation spectra and their assignments are given in Table 3 for the six salts studied, arranged in order of decreasing ^{14}N quadrupole coupling constant. Except for compound (**1f**), ^{14}NH signals were seen in both level-crossing and cross-relaxation spectra; in the latter for (**1f**) they could be identified by comparison with cross-relaxation spectra of the other salts.

Signals from the other ^{14}N nuclei, NMe$_2$ and N(4), were seen reliably only in cross-relaxation spectra. With the ^{14}NH frequencies known, it was possible to identify the other two sets and the most reasonable assignments are given in Tables 4 and 5. Compound (**1b**) gives two sets of ^{35}Cl frequencies, suggesting the presence of two molecules in the crystallographic asymmetric unit, but no splittings were resolved in its ^{14}N spectra.

Finally, ^{35}Cl quadrupole resonance frequencies were detected for all salts, except (**1f**), from C(1)–^{35}Cl, and from the *para*-chlorine substituent in R^1 in (**1b**). These frequencies are given in Table 6. In (**1f**), Cl quadrupole double-resonance frequencies were detected from the ionic chlorine at 2.047 MHz (^{37}Cl) and 2.591 MHz (^{35}Cl), giving a frequency ratio of 1.266, almost exactly equal to the ratio of the electric quadrupole moments (1.269), as expected.[9] No definitely assignable Cl signals were seen from the ClO$_4^-$ ion, nor ^{11}B from BF$_4^-$, except possibly in (**1d**) where lines at 0.581 and 0.505 MHz (ratio 1.15) could be due to ^{35,37}ClO$_4^-$.

Table 1. Analytical data for compounds (**1a**—**f**) and (**3**)[a]

Compd.	C(%)	H(%)	N(%)
(**1a**)	40.7 (40.75)	4.65 (4.7)	12.75 (13.0)
(**1b**)	36.7 (36.8)	4.0 (3.9)	11.55 (11.7)
(**1c**)	51.2 (51.1)	4.7 (4.8)	10.6 (10.5)
(**1d**)	40.6 (40.75)	4.7 (4.8)	12.9 (13.0)
(**1e**)	43.6 (43.9)	5.5 (5.4)	11.7 (11.8)
(**1f**)	55.9 (55.6)	7.1 (7.0)	14.0 (13.9)
(**3**)	53.7 (53.9)	4.7 (4.5)	4.2 (4.5)

[a] Calculated values in parentheses.

Table 2. Selected peak wavenumbers ($\nu_{max.}$/cm^{-1}) in the i.r. spectra of compounds (**1a**—**f**)

Compd.	NH	C=N	C=C	ClO$_4^-$	BF$_4^-$
(**1a**)	3 290	1 640	1 600	1 110br	
(**1b**)	3 290	1 640	1 610	1 100br	
(**1c**)	3 220	1 630	1 605	1 100br	
(**1d**)	3 260	1 645	1 605	1 100br	
(**1e**)	3 200	1 640	1 590		1 070
(**1f**)	3 200	1 640	1 610		

The first problem to be resolved is which of the two structures (**1**) and (**2**) is more consistent with the ^{14}N quadrupole resonance results. Compounds (**1a** and **b**) differ only in the presence of a *para*-chlorine substituent on R^1; the ^{14}N quadrupole parameters assigned to NH in Table 3 change by very little, whereas those assigned to N(4) in Table 4 show a difference of 400 kHz between the quadrupole coupling parameters of the two salts. The substituent effect therefore operates on the nitrogen nucleus labelled N(4) rather than on NH; this is supported by the similar change observed in (**1e**), where however the anion is BF$_4^-$ rather ClO$_4^-$. Structure (**1**), which has been adopted in drawing up Tables 3 and 4, is therefore more likely. This assignment is supported by the ^{14}N quadrupole resonance frequencies observed for compounds (**3**) and (**4**) [Tables 7 (a) and (b)] [^{35}Cl resonance frequencies were also detected for (**4**) and have been included in Table 6]. While the assignments to C(1)=^{14}NMe$_2$ and C(3)=^{14}NMe$_2$ are speculative, the value for N(2) is similar to the values given in Table 4 for N(4), if we bear in mind the difference in substituents. Contrast also the low values of the quadrupole coupling constant and high values of η for (**3**) relative to those given in Table 3, which again suggest that structure (**1**) is more likely than (**2**). These arguments find further support in a more detailed analysis of the ^{14}N quadrupole parameters and their relation to electronic structure.

First, the ^{14}NH frequencies given in Table 3 show clear evidence of hydrogen-bonding effects, which may be emphasized by calculating (Table 8) the individual components q_{xx}, q_{yy}, and q_{zz} of the ^{14}N quadrupole coupling tensor (subject to the usual convention that $|q_{zz}| \geqslant |q_{yy}| \geqslant |q_{xx}|$). The pattern observed is for q_{xx} and q_{zz} to change by almost equal amounts over a range of about 300 kHz with q_{yy} almost constant (to within ±50 kHz); the molecule (**3**) also follows this pattern. Unfortunately, the sign and orientation of the ^{14}N quadrupole components cannot be deduced from these experiments; if however we *assume* that they are similar to those observed in hydrogen-bonded hetero-

Table 3. ^{14}NH Quadrupole parameters for compounds (**1a**—**f**)

Compd.	R^1	R^2	Transition	^{14}N Frequency (MHz)^a Level-crossing	Cross-relaxation*	e^2qQ/h (MHz)	η
(**1f**)	Bu^s	Ph	ν_x		2.342	2.686	0.453
			ν_y		1.717		
			ν_z		0.488		
(**1c**)	*p*-MeC$_6$H$_4$	Ph	ν_x	2.147	2.188	2.498	0.438
			ν_y	1.600	1.635	2.548	0.434
			ν_z	0.546	0.606		
(**1b**)	*p*-ClC$_6$H$_4$	Me	ν_x	2.223	2.200	2.483	0.580
			ν_y	1.502	1.544	2.496	0.525
			ν_z	0.744	0.722		
(**1a**)	Ph	Me	ν_x	2.152	2.174	2.458	0.504
			ν_y	1.535	1.554	2.485	0.499
			ν_z	0.730	0.764		
(**1e**)	*p*-EtOC$_6$H$_4$	Me	ν_x	2.234	2.193	2.468	0.619
			ν_y	1.469	1.481	2.449	0.582
			ν_z	0.703	0.700		
(**1d**)	Me	Ph	ν_x	1.994	2.171	2.234	0.570
			ν_y	1.357	1.391	2.375	0.656
			ν_z	0.588	0.644		

^{a} Peak frequencies corrected for Zeeman shifts.

Table 4. ^{14}N(4) Quadrupole parameters for compounds (**1a**—**f**)

Compd.	R^1	R^2	Transition	^{14}N Frequency (MHz)^a	e^2qQ/h MHz	η
(**1f**)	Bu^s	Ph	ν_x	3.274	4.164	0.112
			ν_y	3.021		
			ν_z	0.316		
(**1c**)	*p*-MeC$_6$H$_4$	Ph	ν_x	3.312	4.198	0.154
			ν_y	2.988		
			ν_z	0.380		
(**1b**)	*p*-ClC$_6$H$_4$	Me	ν_x	3.317	4.140	0.205
			ν_y	2.893		
			ν_z	0.374		
(**1a**)	Ph	Me	ν_x	3.020	3.786	0.191
			ν_y	2.659		
			ν_z	0.392		
(**1e**)	*p*-EtOC$_6$H$_4$	Me	ν_x	3.007	3.734	0.222
			ν_y	2.593		
			ν_z	0.366		
(**1d**)	Me	Ph	ν_x	3.011	3.803	0.167
			ν_y	2.693		
			ν_z	0.299		

^{a} Peak frequencies corrected for Zeeman shifts.

Table 5. ^{14}NMe$_2$ Quadrupole parameters for compounds (**1a**—**f**)

Compd.	R^1	R^2	Transition	^{14}N Frequency (MHz)^a	e^2qQ/h MHz	η
(**1f**)	Bu^s	Ph	ν_x	2.864	3.209	0.530
			ν_y	1.990		
			ν_z	0.866		
(**1c**)	*p*-MeC$_6$H$_4$	Ph	ν_x	2.513	3.093	0.251
			ν_y	2.126		
			ν_z	0.424		
(**1b**)	*p*-ClC$_6$H$_4$	Me	ν_x	2.485	2.818	0.532
			ν_y	1.738		
			ν_z	0.758		
(**1a**)	Ph	Me	ν_x	2.335	2.856	0.271
			ν_y	1.948		
			ν_z	0.483		
(**1e**)	*p*-EtOC$_6$H$_4$	Me	ν_x	2.129	2.609	0.264
			ν_y	1.784		
			ν_z	0.297		
(**1d**)	Me	Ph	ν_x	2.527	2.899	0.486
			ν_y	1.772		
			ν_z	0.934		

^{a} Peak frequencies corrected for Zeeman shifts.

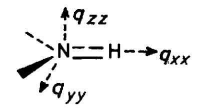
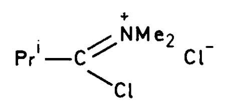


Figure 1. Proposed orientation of the ^{14}NH quadrupole components in a hydrogen-bonded NH group



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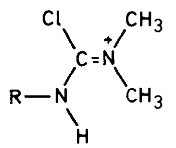

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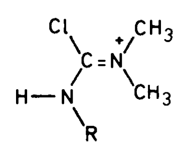
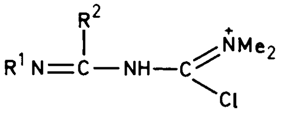


(**7**)

cyclic NH groups, as in Figure 1 (with the signs in brackets in Table 8), then they follow a very similar pattern to the changes observed between vapour and solid state in simple heterocyclic ring systems, in which q_{zz} increases in absolute terms by as much as q_{xx} decreases, q_{yy} remaining roughly constant.[10] Such behaviour is consistent with the transfer of charge density from $2p_\pi$ on N into the σ N–H orbital as the strength of hydrogen bonding increases, consistent with a resonance formulation of the hydrogen bond: $\text{N–H}\cdots\text{X}^- \longleftrightarrow \text{N}^-\cdots\text{H–X}$. We may conclude that the NH group in (**1**) is hydrogen-bonded to the anion, the weakest bonding being to Cl^- in (**1f**) and the strongest to ClO_4^- in (**1d**). In agreement with this, the $^{35}\text{Cl}^-$ frequency observed in (**1f**) (2.591 MHz) is similar to those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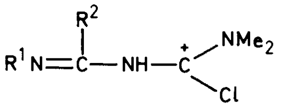
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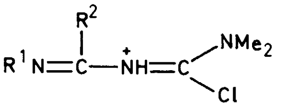
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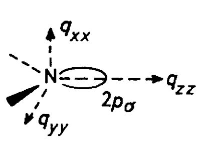

Figure 2. Proposed orientation of the ^{14}N(4) quadrupole components

Table 6. ^{35}Cl Quadrupole resonance frequencies for compounds (**1a**—**e**) and (4)

			^{35}Cl Frequencies (MHz)		
Compd.	R^1	R^2	77 K	195 K	295 K
(**1c**)	p-MeC$_6$H$_4$	Ph	36.537	36.192	36.031
(**1b**)	p-ClC$_6$H$_4$	Me	36.836	36.448	35.842
			36.436	35.730	35.129
			(34.900)	(34.591)	(33.245)^a
			(34.736)	(34.298)	(33.887)^a
(**1a**)	Ph	Me	36.504	35.925	35.345
(**1e**)	p-EtOC$_6$H$_4$	Me	36.887	36.265	35.456
(**1d**)	Me	Ph	36.042	35.497	35.148
(**4**)			36.313	35.910	35.472

^{a} p-^{35}ClC$_6$H$_4$ frequency.

Table 7. ^{14}N Cross-relaxation frequencies (MHz)

(a) N-p-Methoxybenzylideneanilinium perchlorate (3)

ν_x	ν_y	ν_z	e^2qQ/h (MHz)	η
1.839	0.976	0.899	1.877	0.920

(b) 1-Chloro-1,3-bisdimethylamino-2-azapropenylium perchlorate (4)

	C(1)=^{14}NMe$_2$	C(3)=^{14}NMe$_2$	N(2)
ν_x	2.799	3.245	3.519
ν_y	2.374	2.222	3.204
ν_z	0.410	0.108	0.255
e^2qQ/h (MHz)	3.415	3.644	4.482
η	0.219	0.561	0.141

Table 8. ^{14}NH Quadrupole coupling components (MHz)^a

Compd.	q_{xx}	q_{yy}	q_{zz}
(**1f**)	0.735	1.951	(−)2.686
(**1c**)	0.712	1.812	(−)2.523
(**1b**)	0.558	1.932	(−)2.490
(**1a**)	0.616	1.856	(−)2.472
(**1e**)	0.491	1.968	(−)2.459
(**1d**)	0.445	1.861	(−)2.304
(3)	0.075	1.803	(−)1.877

^{a} Average values, except for (**1f**) and (3)

Table 9. N(4) Quadrupole coupling components (MHz)

Compd.	q_{xx}	q_{yy}	q_{zz}
(**1f**)	1.849	2.135	(−)4.164
(**1c**)	1.776	2.422	(−)4.198
(**1b**)	1.646	2.494	(−)4.140
(**1d**)	1.584	2.220	(−)3.803
(**1a**)	1.531	2.255	(−)3.786
(**1e**)	1.453	2.281	(−)3.734

reported for other hydrogen-bonded chlorides such as pyridinium hydrochloride (2.762 MHz)[11] and cystosine hydrochloride (2.702 MHz).[12]

Turning to the other groups in the molecule, we note a strong resemblance to the Vilsmeier–Haack and Viehe reagents; (**5**) has a ^{35}Cl frequency for the covalently–bonded atom of 36.45 MHz at 77 K,[13] to be compared with a mean frequency of 36.5 ± 0.4 MHz for the compounds in Table 6. If Pr^i in (**5**) is replaced by C$_6$H$_5$, the ^{35}Cl frequency rises to 37.05 MHz, and by another Cl, to 39.74 MHz. These observations suggest that little if any change occurs in charge transfer to the $-\mathrm{CCl{=}\overset{+}{N}Me_2}$ group in (**1a**—**f**) from the rest of the cation, as substituents at N(4) or hydrogen bonding at N(2) are varied. In agreement with this conclusion, there is poor correlation between the ^{14}N(2) H quadrupole parameters in Table 3 and those of $\mathrm{C{=}^{14}\overset{+}{N}Me_2}$ in Table 5. As far as the latter are concerned, the most noteworthy feature is the tendency of the ^{14}N asymmetry parameters to fall into two groups, one for molecules (**1f**, **b**, and **d**) in which its average value is 0.52, and the other for (**1c**, **a**, and **e**) with an average value of 0.26, which suggests a steric effect according to which configuration [(**6**) or (**7**)] is adopted in the solid state. The low asymmetry parameter assigned to the C(1)=^{14}NMe$_2$ nitrogen atom in (**4**) is consistent with molecules (**1a**, **c**, and **e**) having configuration (**7**) and (**1b**, **d**, and **f**) configuration (**6**), but this conclusion needs further verification. The assignment of $\mathrm{C(1){=}\overset{+}{N}Me_2}$ in Table 7 is made mainly on the grounds that its ^{14}N quadrupole coupling constant is closer to the values for (**1a**—**f**) in Table 5.

Of the three possible resonance structures (A)—(C) for the cation, structure (A) appears to contribute most to the hybrid, according to our interpretation of the ^{14}N quadrupole coupling data. We have therefore named the salts according to structure (A).

Finally, N(4) shows electronic effects due to both substituents R^1 and R^2. Unfortunately, the orientation of the ^{14}N quadrupole coupling tensor at this nucleus is not known with any certainty; as in the azoles,[14] q_{zz} is likely to lie roughly along the direction of the $2p_\sigma$ lone pair and (e^2qQ/h) is negative; from the magnitudes observed, it is reasonable to assume that q_{xx} lies perpendicular to the CNC plane, as in gaseous imidazole,[15] giving the orientation in Figure 2. As Table 9 shows, the major change is for q_{xx} and q_{zz} to vary in parallel, with q_{yy} *roughly* constant, and with q_{xx} becoming less positive as q_{zz} becomes more positive (note that the order of compounds is different from that in Table 8). If Figure 2 is correct and the inferred signs in Table 9 are also justified, then this order implies simple transfer of charge from $2p_\sigma$ to $2p_\pi$ as we go down Table 9 from (**1f**) to (**1e**), the highest values of $2p_\pi$ being observed in (**1e**) with R^1 = p-EtOC$_6$H$_4$, and the lowest in (**1f**) with R^1 = Bu^s. This is the expected order of π-conjugative effects from the R^1

substituent, but it is interesting to note the similar quadrupole components observed for **(1a)** and **(1d)** in which the substituents R^1 (CH_3) and R^2 (C_6H_5) have been simply interchanged, suggesting that aromatic substituents at both positions 4 and 3 can bring about this transfer.

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