

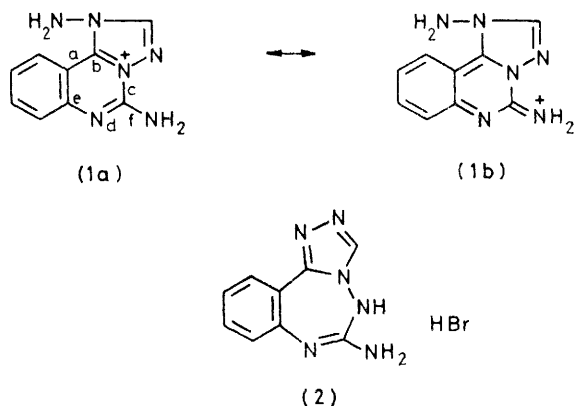
X-Ray Crystallographic and Infrared Spectroscopic Evidence for the Electronic Structure of the 1,5-Diamino-1*H*-1,2,4-triazolo[1,5-*c*]quinazolinium Cation

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The crystal structure of the title cation (1) shows it to possess a system of strongly localised alternant double bonds which can be interpreted in terms of a dominant pseudo-quaternary canonical form. Its i.r. spectrum contains a doublet near $1\ 700\text{ cm}^{-1}$ which is interpreted, on the results of deuteration, as $\nu(\text{C}=\text{N}^+)$ coupled with $\delta(\text{NH}_2)$ and with other ring modes. The electron distribution revealed by both techniques helps to explain the high and localised reactivity of the cation.

We have previously reported¹ that the reaction of cyanogen bromide with 4-amino-3-(2-aminophenyl)-4*H*-1,2,4-triazole yields 1,5-diamino-1*H*-1,2,4-triazolo[1,5-*c*]quinazolinium (1) bromide and not the expected isomeric triazepine (2). We have now determined the X-ray crystallographic data for (1) nitrate. Certain features of the structure so revealed are unexpected, as are the solid-state i.r. spectrum of the bromide, and the



unusual reactions it undergoes.² We now show how these apparent anomalies add up to a consistent pattern of chemical structure and reactivity.

EXPERIMENTAL

Crystallography.—Since we were unable to grow suitable crystals of (1) bromide, the structure determination was carried out on the nitrate. **Crystal data.** $\text{C}_9\text{H}_9\text{N}_6^+\cdot\text{NO}_3^-$, $M = 263.2$. Monoclinic, $a = 15.53(1)$, $b = 6.011(3)$, $c = 15.84(1)\text{ \AA}$, $\beta = 131.0(1)^\circ$, $U = 1\ 115(1)\text{ \AA}^3$, $D_m = 1.56$, $Z = 4$, $D_c = 1.568\text{ g cm}^{-3}$. Space group $P2_1/c$. Mo- K_α radiation, $\lambda = 0.7107\text{ \AA}$; $\mu(\text{Mo-}K_\alpha) = 1.335\text{ cm}^{-1}$

After preliminary X-ray photographs to determine space group and crystal quality, accurate cell dimensions and intensity data were measured on a Picker card controlled four-circle diffractometer ($2\theta \leq 45^\circ$) with niobium-filtered Mo- K_α radiation. The trial structure was determined by direct methods (MULTAN) and refined by least squares by use of 908 reflections with intensity $I > 3.5\sigma(I)$. After five cycles, with $R\ 0.115$, an electron-density difference synthesis was calculated. The largest excursion of $\pm 0.8e$ occurred near the nitrate ion, indicating anisotropic thermal motion; seven peaks of $+0.3$ to $+0.5e$ were in positions expected for hydrogen atoms. Contributions from these

atoms were included (without refinement) in further least-squares cycles, in which the atoms of the nitrate ion were given anisotropic thermal factors. Refinement converged at $R\ 0.087$.

TABLE I
Final fractional co-ordinates ($\times 10^4$) *

	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	2 961	4 284	5 245
C(2)	2 839	6 137	5 700
C(3)	3 744	7 541	6 361
C(4)	4 769	7 186	6 596
C(5)	4 895	5 382	6 161
C(6)	3 991	3 868	5 471
C(7)	3 323	0 702	4 358
C(8)	2 091	2 694	4 504
C(9)	0 593	0 589	3 413
N(1)	4 160	2 085	5 048
N(2)	2 284	1 025	4 092
N(3)	1 344	-0 323	3 389
N(4)	1 006	2 406	4 071
N(5)	0 454	3 785	4 321
N(6)	3 402	-1 002	3 883
N(7)	1 726	4 076	1 821
O(1)	1 995	5 009	2 665
O(2)	0 998	2 674	1 389
O(3)	2 165	4 316	1 463
H(2)	2 155	6 381	5 539
H(3)	3 661	8 763	6 658
H(4)	5 379	8 172	7 061
H(5)	5 584	5 111	6 330
H(6)	4 203	-1 415	4 098
H(7)	2 833	-2 251	3 425
H(9)	-0 180	-0 205	2 962

* Estimated standard deviations are listed in Supplementary Publication (see text).

Final atomic positional parameters are given in Table I, and bond lengths and angles in Figure 1. All the carbon

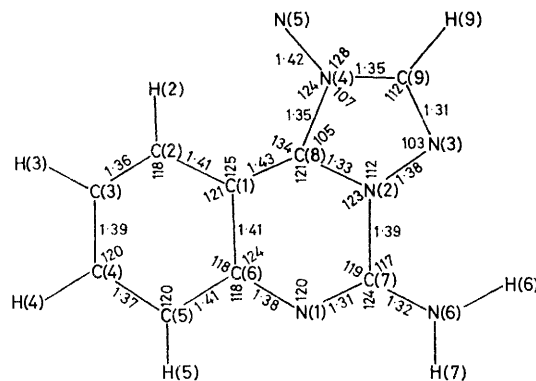


FIGURE 1 Bond lengths (\AA), $\sigma\ ca. 0.01$, and angles ($^\circ$), $\sigma\ ca. 0.5$, for the cation (1) showing the atom numbering

and nitrogen atoms of the cation lie within 0.05 Å of the mean plane defined by them. Final observed and calculated structure factors, atom thermal parameters, and detailed estimated standard deviations relating to Table 1 are listed in Supplementary Publication No. SUP 22378 (15 pp., 1 microfiche).*

Spectroscopy.—The i.r. spectra of (1) bromide in its *N*-protonated and *N*-deuteriated forms are shown for Nujol mulls in Figure 2. Selected data for both forms appear in Table 2. Deuteriation was carried out by dissolving (1) bromide in deuterium oxide and evaporating the solution to dryness on a freeze drier; a Nujol mull was prepared from the resulting solid under dry-box conditions. Spectra were obtained on a Perkin-Elmer 457 double-beam spectrometer.

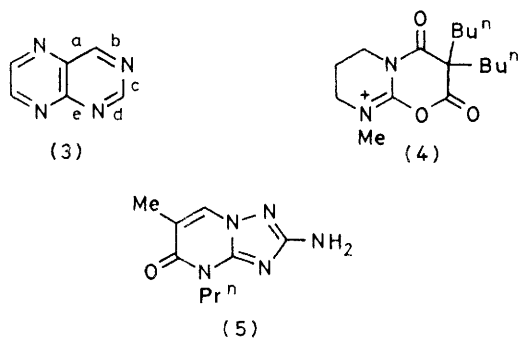
TABLE 2
I.r. data (Nujol) on (1) bromide before and after deuteriation

NH Form	ND Form	Ratio NH:ND	Assignment
3 285	2 475	1.325	$\nu_{as}(\text{NH}_2)(\text{N})$
3 185	2 390	1.33	$\nu_s(\text{NH}_2)(\text{N}) + \nu_{as}(\text{NH}_2)(\text{C})$
3 075	2 280	1.35	$\nu_s(\text{NH}_2)(\text{C})$
1 708	1 687	<i>a</i>	} $\nu(\text{C}=\text{N})(\text{b})$
1 691	1 669	<i>a</i>	
1 646	1 418	<i>a</i>	$\delta(\text{NH}_2)(\text{C})$
1 618	1 622		$\nu(\text{Ph})$
1 597	1 251	1.28	$\delta(\text{NH}_2)(\text{N})$
1 571	1 581	<i>a</i>	} $\nu(\text{C}=\text{N})(\text{d})$
1 553	1 564	<i>a</i>	
1 524	1 529		Triazole $\nu(\text{C}=\text{N})$
1 490	1 489		$\nu(\text{Ph})$
1 245	1 222	<i>a</i>	$\nu(\text{CN})(\text{c})$
1 209	1 051	<i>a</i>	$\nu(\text{CN})(\text{f})$
1 075	852	1.27	$\tau(\text{NH}_2)(\text{N})$
1 028	831	1.24	$\tau(\text{NH}_2)(\text{C})$

* These vibrations are coupled so their assignment is approximate (see text).

DISCUSSION

The outstanding feature of this molecule as revealed by *X*-ray crystallography is its high degree of bond fixation. This is particularly noticeable in the pyrimidine ring, where lengths of 1.33 and 1.31 Å for bonds (b) and (d) compare with 1.28 and 1.34 Å for the equi-



valent bonds in pteridine (3).³ In both molecules, the alternant bonds (a), (c), and (e) are much longer than their neighbours. A mild degree of bond fixation in the sense implied by formula (3) is already present in naphthalene,⁴ but this is a much more extreme effect. One consequence for pteridine (3) and many quinazolines is their ready covalent hydration across bond (b),⁴ and in similar fashion the ring transformation of (1) is

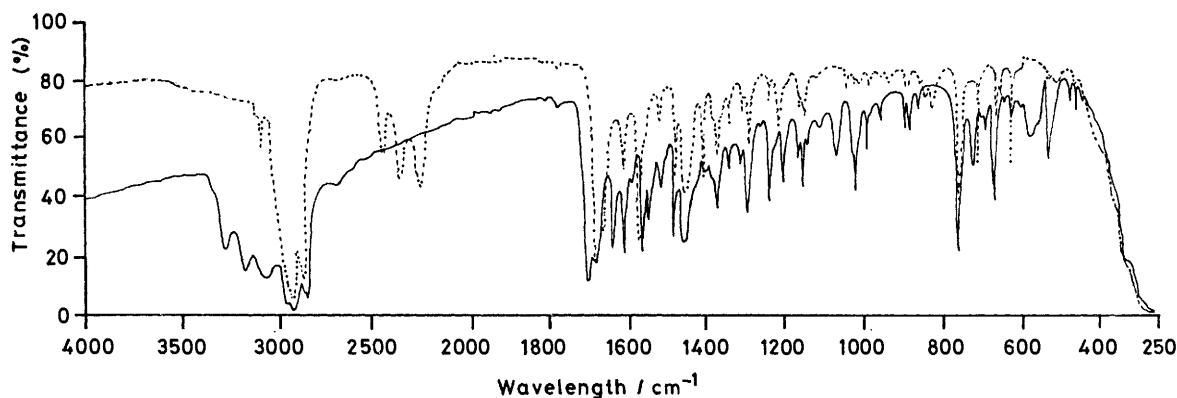
initiated by attack of hydroxide ion at the equivalent position.²

This evidence suggests that molecule (1) is a resonance hybrid of the canonical forms (1a) and (1b), with (1a) predominating. The quinonoid nature of (1b) is expected⁵ to diminish the importance of its contribution to the structure. This conclusion is not contra-indicated by the shortening observed in bond (f), which is normal for amino-heterocycles⁶ and probably results from the increased *s*-character of C–N linked to NH₂.

We now adduce i.r. spectroscopic evidence for these propositions. The outstanding feature in the i.r. spectrum of (1) is a very strong doublet close to 1 700 cm⁻¹ which, if the molecular formula had contained oxygen, might well have been mistaken for carbonyl. Simple pyrimidine ring modes resemble in position those of benzene;⁷ however, C=N⁺ resembles carbonyl electronically, and the appropriate band of (4) occurs⁸ at 1 664 cm⁻¹. Such 'pseudo-carbonyls' are not uncommon, though the present case represents the highest such frequency we have encountered.

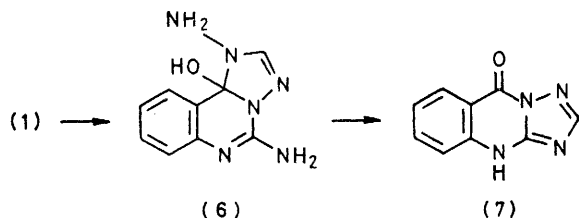
Deuteriation throws considerable light on the nature of the i.r. modes. Pure NH vibrations are readily identified since they move on deuteriation to approaching the theoretical⁹ extent: the stretching, $\nu(\text{NH}_2)$, and in-plane wag, $\tau(\text{NH}_2)$, vibrations are assigned this way (see Table 2). Also we assign the weak band at 1 597 cm⁻¹ to the in-plane scissors vibration, $\delta(\text{NH}_2)$, of the isolated NH₂–N group. Similarly, benzenoid ring vibrations and the isolated $\nu(\text{C}=\text{N})$ of the triazole ring are readily assigned since they are insensitive to deuteriation. There remain a series of bands at 1 708, 1 691, 1 646, 1 571, 1 553, 1 245, and 1 209 cm⁻¹, all of which are deuteriation-sensitive in some degree. That at 1 646 cm⁻¹ moves most, so might naively be assigned to $\delta(\text{NH}_2)$ for the amino-group on carbon. This view is too simple: its frequency is anomalously high, and its shift to 1 418 cm⁻¹ is far too small for a pure vibration⁹ (NH:ND 1.16). At the same time, the doublet near 1 560 cm⁻¹ shows an anomalous rise in frequency. We believe the explanation to lie in coupling between $\delta(\text{NH}_2)$ and the neighbouring $\nu(\text{C}=\text{N})$ of the more or less localised double bond (d), which is broken on deuteriation so that $\nu(\text{C}=\text{N})$ then rises. Such coupling is known in the guanidinium cation,¹⁰ where $\delta(\text{NH}_2)$ and $\nu(\text{C}=\text{N})$, both expected near 1 600 cm⁻¹, couple to give new vibrations close to 1 650 and 1 550 cm⁻¹. We have observed the same phenomenon in a number of amino-heterocycles containing localised double bonds;¹¹ an example is the triazolopyrimidone (5),¹² where strong bands at 1 617 and 1 549 cm⁻¹ (in chloroform solution) are replaced by new bands at 1 567 and 1 184 cm⁻¹, an overall ratio $\Sigma\text{NH}:\Sigma\text{ND}$ of 1.35. The remaining deuteriation-sensitive bands of (1), at 1 245 and 1 209 cm⁻¹, we assign essentially to the $\nu(\text{CN})$ of bonds (c) and (f), in that order, since the latter moves more on deuteriation. Its relatively low frequency is further evidence against the predominance of

* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1978, Index issue.



canonical form (1b). The overall ratio $\Sigma\text{NH} : \Sigma\text{ND}$ for these seven vibrational modes, by the Teller-Redlich product rule,⁹ is 1.38, *i.e.* approaching the theoretical.

We may therefore assign with some confidence the bands near 1700 and 1560 cm^{-1} to modes associated with the essentially localised double bonds (b) and (d) respectively. Each is a doublet, and since this feature survives deuteration it is not plausibly explained as Fermi resonance. Possibly it results from degeneracy, *i.e.* from mixing with modes due to the adjacent bonds (a) and (e) which must also possess some double-bond character [*cf.* canonical form (1b)]. If so, these coupled vibrations comprise almost every in-plane mode of the aminopyrimidine moiety.



On this simplistic approach the most electron-deficient position in the molecule is that with the highest double-bond frequency, *i.e.* bond (b). This is borne out by its chemical reactivity: (1) on treatment with alkali

gives the triazoloquinazolone (7), most plausibly *via* the adduct (6).² No free base can be isolated.

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