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THE INFRARED SPECTRA OF FUSED 1,2,4-TRIAZIN-5-ONES

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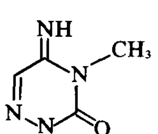
Abstract—The IR spectra of a number of fused 1,2,4-triazin-5-ones have been studied and the relevance of the results to triazinone tautomerism is discussed.

It is now generally accepted that in most cases amino-groups in heterocyclic compounds exist as such, any imino-tautomer being present only in amounts too small to be detected.[1] Exceptions to this rule include triazinones which would otherwise require a formal -N=N- bond in their structure and this has led to the generalisation that in azines such a bond is avoided,[2,3] leading to otherwise unexpected tautomers being present as a result, as in **1**[4] and **2**.[5]



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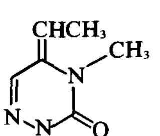

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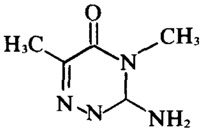
One explanation considered by Pitha *et al*[2] is that in-plane lone pair interactions of sp^2-hybridised nitrogen atoms lead to the destabilisation of an otherwise conjugated system but they discounted this on the evidence that **3** exists as such and not as the imino-tautomer **4**. We have recently studied the IR spectra of a number of fused 1,2,4-triazinones and our results show that the imino-tautomers of such systems are capable of existence.



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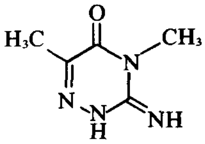

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EXPERIMENTAL

The preparation of **a** and **e** (see Table 1) have been reported previously.[6] The preparation of the other compounds, with the exception of **p**, is a modification of the method of Brugger and Korte[7] and is illustrated by the preparation of **b**. All compounds gave satisfactory analytical data. Melting points are uncorrected.

3,8-*Dimethyl*-7,8-*dihydro*-6*H*-*imidazo*[2,1-*c*][1,2,4]-*triazin*-4-*one* **b**. A soln of 2-hydrazino-1-methyl-Δ²-imidazoline hydriodide[6] (2·42 g) and ethyl pyruvate (1·16 g) in ethanol (20 ml) was allowed to stand at room temperature for 20 h. The soln was then evaporated to dryness, the residue taken up in water (25 ml), basified with solid sodium carbonate and the suspension was extracted with chloroform (3 × 25 ml). Evaporation of the dried chloroform extracts yielded a solid which was heated under reflux with glacial acetic acid (40 ml) for 2 h. The soln was evaporated to dryness and the residue given a further base treatment as above and the resulting solid was recrystallised from ethyl acetate/petrol (60–80) to yield the product (1 g), mp 102–3° (Found: C, 50·6; H, 6·0; N, 33·7. $C_7H_{10}N_4O$ requires C, 50·6; H, 6·0; N, 33·75%).

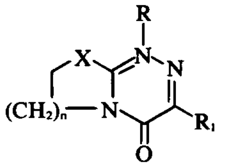
3-*Methyl*-7,8,9,10-*tetrahydro*-6*H*[1,2,4]-*triazino*[4,3-*a*] *azepin*-4-*one* **p**. A soln of ε-caprolactam-O-methylether (6·35 g) in ethanol (50 ml) was treated with 100 per cent hydrazine hydrate (2·5 g) and the mixture stood at room temperature for 2 h. Ethyl pyruvate (5·8 g) was then added and the mixture stood for a further 20 h. Evaporation to dryness yielded an oil which was heated for 3 h under reflux with glacial acetic acid (50 ml). Evaporation to dryness yielded a gum which was dissolved in a little isopropanol and the soln treated with isopropanol saturated with HCl to yield the hydrochloride of the product. Recrystallisation from ethanol/ether and recovery of the free base by normal procedures yielded **p** (2 g), mp 80–81° from ether (Found: C, 60·2; H, 7·3; N, 23·2 $C_9H_{13}N_3O$ requires C, 60·4; H, 7·3; N, 23·2%).

Spectra. The IR spectra were measured on a Perkin Elmer 457 double beam grating spectrophotometer in chloroform and nujol. The results are given in the Table, the chloroform frequencies being reported first in each case. ν_1 is the frequency of the ring carbonyl, ν_2 that of the ring junction C=N bond.

DISCUSSION

From the data given in the Table for the chloroform solns there is, in the case of n = 1, a clear relationship between the frequency of the ring carbonyl group (ν_1) and the frequency of the C=N bond at the ring junction (ν_2). Where the double bond is contained within the triazinone ring, i.e. the fully conjugated system, the difference in their frequencies is of the order of 83–92 cm^{-1} (compounds **a**–**c**). This value rises to well over 100 cm^{-1} in compounds **h**–**j**, due to a fall in ν_2, probably caused by an effect similar to that responsible for the fall in frequency of the carbonyl group of thiol esters.[8] Where the C=N bond is exocyclic to the triazinone ring, i.e. the imino-form, compound **d**, the difference in frequency falls to 45 cm^{-1}. When these data are applied to **e**–**g**, which are capable of amino-imino-tautomerism, it can be seen that

Table 1

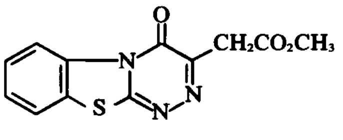


	n	X	R	R$_1$	m.p°.c.	ν_1 cm^{-1}	ν_2 cm^{-1}	$\Delta\nu$ cm^{-1}
a	1	NCH$_3$	—	CH$_2$CO$_2$CH$_3$	98–9	1685 s	1593 vs	92
						1681 s	1612 s	69
b	1	NCH$_3$	—	CH$_3$	102–3	1681 s	1598 vs	83
						1668 s	1575 s	93
c	1	NCH$_3$	—	Ph	184–5	1679 s	1591 vs	88
						1672 vs	1611 vs	61
d	1	N	CH$_3$	CH$_3$	142	1687 s	1642 vs	45
						1683 s	1643 vs	40
e	1	NH	—	CH$_2$CO$_2$CH$_3$	202	1684 s	1600 s	84
						1686 s	1606 s	80
f	1	NH	—	CH$_3$	291–2	1680 s	1602 vs	78
						[1670 s	1622 vs	48]
						1682 s]	1604 vs	78]
g	1	NH	—	Ph	210	1681 s	1597 vs	84
						1678 s	1614 vs	64
h	1	NPh	—	CH$_3$	225–7	1685 s	1568 vs	117
						1690 vs	1584 vs	106
i	1	S	—	CH$_3$	171–2	1686 s	1541 m	145
						1681 vs	1546 vs	135
j	1	S	—	Ph	134–5	1687 s	1525 s	162
						1686 vs	1530 ms	156
k	2	NH	—	CH$_3$	280	[1678 s	1611 ms	67]
							1575 vs	103]
						1668 s	1619 vs	49
l	2	NH	—	Ph	267	1675 m	1573 s	102
						1678 s	1613 vs	65
m	2	NMe	—	CH$_3$	133	1667 s	1554 vs	113
						1661 vs	1560 vs	101
n	3	NH	—	CH$_3$	228	1677 s	1572 ms	105
						1673 vs	1606 s	67
o	3	NH	—	Ph	224	[1678 s	1559 s	119]
							1588 m	90]
						1680 s	1588 s	92
p	3	CH$_2$	—	CH$_3$	80–1	1673 vs	1564 s	109
						1665 vs	1565 m	100

the amino-tautomer is the preferred form. More significant are the solid state spectra. The frequency-difference correlation is not quite so exact but sufficiently so to allow assignment of the same structures to **e** and **g** as in soln. However it is clear that in the case of **f** both forms are isolable in the solid state although no method has been developed to yield the tautomer of choice. Which form is isolated is a matter of chance. It is significant to note here that Lempert[9] considered alternative tautomeric forms for this compound and concluded that the structure of the compound he isolated had the amino-tautomeric form.

Similar relationships hold where n = 2 and 3. Here the difference in frequencies is somewhat greater, particularly in soln. It is clear that in the solid state compounds **k**, **l**, **n** and **o** exist as imino-tautomers. Only in soln does the amino-tautomer predominate, in compounds **k** and **o** in equilibrium with the imino-tautomer.

Such relationships can be applied to more complicated



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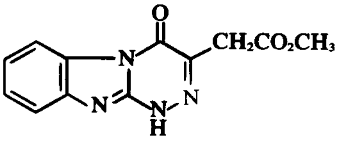

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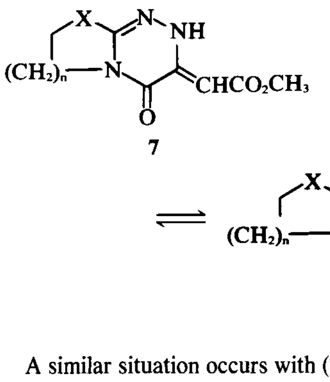
systems. In **5**[6] ν_1 and ν_2 are 1690 cm^{-1} and 1529 cm^{-1} respectively, a difference of 161 cm^{-1}. In **6**[6] the corresponding frequencies are 1694 cm^{-1} and 1643 cm^{-1} giving a difference of 51 cm^{-1}. These data are in complete agreement with those given in the Table.

In discussing the stability of amino-triazinones we feel two opposing factors must be brought into consideration. One is conjugation which would impart a degree of heteroaromatic stability upon the molecule. The opposing factor is the in-plane lone pair interactions of neighbouring sp^2-hybridised nitrogen atoms considered by Pitha *et al.*[2] Such interactions would encourage the molecule to take up a fine structure avoiding such a situation. Our results show these factors to be finely balanced and slight energy differences could lead to the formation of one tautomeric structure at the expense of the other. Where a structure would require a formal -N=N- bond the lone pair interactions are greatest and this structural element is avoided. Where a longer single bond joins the two atoms these interactions are reduced and other factors influencing the total energy come into effect in deciding the tautomeric state of the molecule.

One such factor is hydrogen bonding. In his work on the reaction of cyclic amidrazones with dimethyl acetylenedicarboxylate, Wamhoff[10] isolated the triazinones (**7**; X = CH_2). Only in soln was the conjugated system (**8**; X = CH_2) observed when the equilibrium **7**$\rightleftharpoons$**8** was set up. The state of the equilibrium is solvent dependent; in methanol, with considerable hydrogen bonding involving the solvent and the ester carbonyl group, **8** is preferred but in non-polar media the proportion of **7** is significantly greater.



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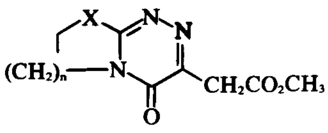

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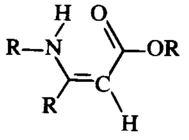
A similar situation occurs with (**7**; X = S, n = 1) and (**8**; X = S, n = 1), with the difference that in this case each tautomer is capable of a separate existence.[6] A soln of (**7**; X = S, n = 1) in methanol deposits (**8**; X = S, n = 1) whereas acetone solns of the latter deposit the former on standing.[11] Here hydrogen bonding between acetone and N-H swings the balance in favour of (**7**; X = S, n = 1).



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One of us[12] has devised a system whereby the carbonyl and C=C frequencies of systems **9** in soln may be predicted. When applied to **8** (X = S, n = 1) the predicted frequencies are 1655 cm^{-1} and 1610 cm^{-1} respectively, very close to the observed frequencies in chloroform (1652 cm^{-1} and 1603 cm^{-1}). This shows there is little net drift of electrons to or from this portion of the molecule (**8**; X = 5, n = 1) in chloroform thus the nominal loss of conjugation affects little the electron distribution of the molecule. This evidence is reinforced by the almost invariant value of the carbonyl frequencies in soln of the triazinones studied.

CONCLUSION

Two opposing factors operate in deciding the tautomeric state of triazinones, namely in-plane lone pair interactions of neighbouring sp^2 hybridised nitrogen atoms and the stability of a conjugated system. For triazinones the latter is likely to be small since it is known that aza-substitution progressively reduces resonance energy.[13] The situation is therefore finely balanced and other external factors can influence the fine structure taken up by these molecules.

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