Systematic Analysis of Substituent Effects on the ^{13}C Chemical Shifts of the Ring Carbons in Trimethyl-cyanurates and -thiocyanurates

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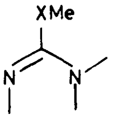
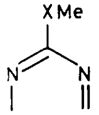
The carbon-13 n.m.r. spectra of 23 of the 24 possible isomers of *O*- and *S*-substituted trimethyl-*s*-triazine are reported. The 69 chemical shifts of the ring carbons distributed over a 42.4 p.p.m. range have been assigned on the basis of a classification into 16 groups obtained by combining a number of structural characteristics which identify the different carbon sites. This assignment allows a prediction of the resonance peaks of the only isomer not synthesized so far. Shielding and deshielding effects of substituents modifying the charge density at each carbon are shown to combine and determine the actual distribution of chemical shifts into 16 classes each made of groups of three or four peaks and spanning a frequency range 3—8 p.p.m. wide. These groups were found to correlate with the π-electron delocalisation energy, to the π-atomic orbital electron densities, and to the trend observed in thermal isomerisations and methanolysis.

The synthesis of 23 of the 24 possible methylated isomers of cyanuric acid and of mono-, di-, and tri-thiocyanuric acid (Figure 1a) has been previously reported.[1,2] The behaviour of the OMe derivatives in thermal isomerisation and of the SMe derivatives in nucleophilic substitution (by methanolysis) forms the three simple patterns shown in Figure 1b, i-1 and i-2 for the two OMe isomerisation reactions and s for the methanolytic substitution.

It was then possible to identify two molecular regions which show different behaviour. Both isomerisation and substitution reactions occurred spontaneously and went to completion under very mild conditions with isomers having region (I). The same reactions required very drastic conditions to occur with isomers having region (II). Consequently, regioselective thermal isomerisation and methanolysis were possible whenever both regions were present in the same molecule.



(I)



(II)

X = O, S

This behaviour was tentatively explained along the lines proposed several years ago by Sheferd and Fedrik;[3] the difference between regions (I) and (II) could be due to a different electron density at the carbon atoms of the *s*-triazine ring.

The work reported here has been carried out in order to obtain some experimental evidence on the electron distribution in the ring carbon atoms through the study of their chemical shifts. Indeed the relationship found by Karplus and Pople[4] for the local paramagnetic contribution to the shielding constant shows a dependence on the effective nuclear charge at the nucleus considered; moreover a linear dependence of aromatic carbons chemical shifts on local π-electron densities was reported.[5,6]

In the present paper the ^{13}C n.m.r. spectra of 23 out of the 24 possible trimethyl derivatives of cyanuric and mono-, di-, and tri-thiocyanuric acids are reported, and a procedure for peak assignment presented. The correlations between chemical shifts and calculated charge densities are examined and the relative importance of a number of structural characteristics in affecting the chemical shifts of ring carbons is systematically related to their influence in modifying the charge distribution in the *s*-triazine ring. Finally some conclusions are drawn on the correlation between the chemical shifts and the behaviour observed in the thermal isomerisation and methanolysis processes.

Results

Spectral Data.—The compounds considered, and the chemical shifts of their ring and methyl carbons, are reported in Table 1. The chemical shifts of the heterocyclic ring carbons of 23 of the 24 listed compounds [isomer (**27**) has not been synthesized as yet] vary from δ 145.0 to 187.4 p.p.m., the absolute range being 42.4 p.p.m., and contain 69 signals. Their assignment results from a systematic procedure developed for the classification of the ring carbon atoms of the whole set of compounds and is consistent with the analysis of chemical shifts reported below.

The chemical shifts of the methyl carbons vary from δ 13.2 to 57.4 p.p.m.; their assignment was fairly obvious. They fall into three non-overlapping ranges: SMe peaks at δ 13.2—15.7 p.p.m., NMe peaks at δ 28.4—45.0 p.p.m., and OMe peaks at δ 54.7—57.4 p.p.m.

Procedure for Peak Assignment: Ring Carbon Classification and Peak Analysis.—The conventional numbering of the *s*-triazine ring was found inadequate for unambiguous identification of the ring carbon atoms of the compounds under study, and for the analysis and global presentation of data. A systematic procedure was therefore worked out which allowed the ring carbon classification, the peak assignment, and the analysis of the chemical shifts to be carried out *in parallel*. The starting point of the procedure was the identification of four structural characteristics needed to define, both geometrically and chemically, each carbon site: (1) the nature of its extranuclear substitutents; (2) the valence states of the adjacent nitrogen atoms; (3) the geometric arrangement of the *meta*- and *para*-substitution; and (4) the nature of the two *meta*-substituents.

All the geometrical, chemically compatible, combinations of

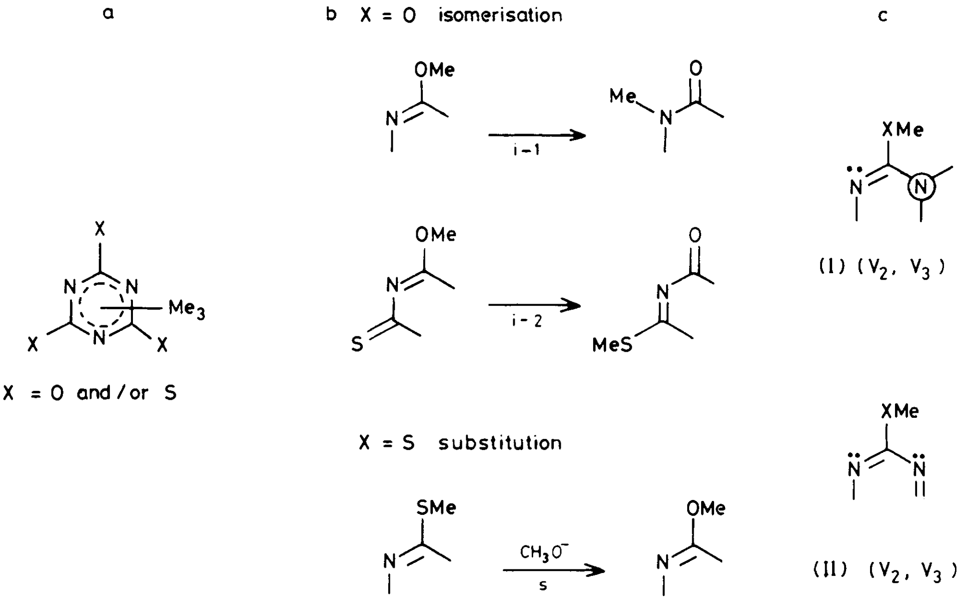


Figure 1. a, General formula of the 24 trimethyl(thio)cyanurates (see Table 1). b, General reactions of the C–XMe groups in the thermal isomerisations i-1 and i-2 for the methoxy (X = O) derivatives, and in the substitution reactions for the thiomethyl (X = S) derivatives. c, Molecular regions (I) and (II) for the reactive C–XMe groups (X = O or S) characterised by the valence states of the adjacent nitrogen atoms; the nitrogen valence states V_2 and V_3 (see text) are identified in this and following Figures and Tables as $\ddot{N}$ and Ⓝ

the first three characters allowed the generation, in successive steps, of 16 classes of carbon sites [see section (a)]. At the same time, the study of the effects of each structural characteristic on the ring carbon polarisation allowed the actual chemical shifts to be accounted for in terms of the combination of the mentioned effects on the charge density of ring carbons [see section (b)].

The complete peak assignment was therefore the self-consistent result of the stepwise procedure for the classification of ring carbons and peak analysis.

(a) The classification of ring carbons was performed along the steps reported in Table 2. The four extranuclear substituents R (R = =S, SMe, OMe, and =O) define four main classes of carbons each one splitting into two when the valence states of the adjacent nitrogen atoms are considered. The correct identification of these valence states is an essential point of this global analysis. Using Mulliken's notation (*tr* for trigonal σ-hybrid orbitals, π for the $2p\pi$ atomic orbitals, and the exponent showing the number of electrons assigned to each one) they are: N (tr^2, tr^1, tr^1, π^1; V_2), contributing one π-electron to the ring pool, and hereafter called V_2; N (tr^1, tr^1, tr^1, π^2; V_3), contributing two π-electrons to the ring pool, and hereafter called V_3. The pair of nitrogen atoms adjacent to a C=X carbon (X = O or S) can either be V_2, V_3 or V_3, V_3; whereas those adjacent to a C–XMe carbon can either be V_2, V_2 or V_2, V_3 (Figure 1c). Consequently the combination of R substituents with the four independent valence state alternatives generate eight ring carbon sites differing in their structural and electronic features.

There are moreover four possible geometric arrangements of *meta-para*-substitution with respect to the *s*-triazine ring, which gave rise to the molecular frameworks identified in Table 2 as A—D when they are combined to a site with a C=X ring carbon, and as A′—D′ when they are combined to a site with a C–XMe carbon (otherwise A = A′, *etc.*). Their selective, two-by-two combination with the eight sites above makes up the molecular framework and therefore provides 16 different sites, and hence the classes where the corresponding ring carbon atoms fall.

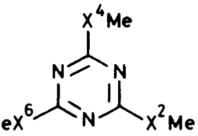
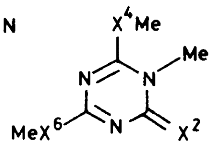
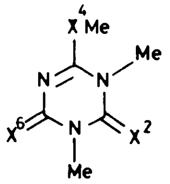
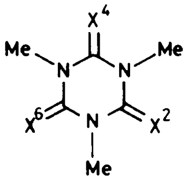
(b) On the basis of the present classification, peak analysis for assignment was performed by starting with unambiguous peaks for ring carbons belonging to molecules of general formula M and Q (see Table 1) and then considering all the other peaks in a sort of iterative process for the best fit. This left a small number of unassigned peaks. Complete assignment was achieved by separately analysing the effectiveness of each structural character in modifying the charge distribution at each carbon site and considering the effects of the fourth structural character mentioned above (see Disscussion section).

In the assignment the criteria adopted for the formal classification of ring carbons were shown also to be the relevant factors responsible for the actual shielding at each carbon site. In line with the classification adopted the signals are distributed into the four ranges named according to the substituent R, the C=S, C–SMe, C–OMe, and C=O ranges, occupying successive, although overlapping, frequency fields 15.5, 22.7, 21.8, and 11.4 p.p.m. wide, respectively. Each range splits first into two sub-ranges, of approximately the same width, in relation to the valence states of the adjacent nitrogen atoms and, then, into four groups, also of about the same width corresponding to the four possible *meta-para*-arrangements previously examined. This sequential combination of the interplay between structural characteristics, shown in Figure 2, generates the 16 groups, each containing three or four signals distributed within limited ranges whose width varies from 3 to 8 p.p.m., corresponding to the 16 carbon sites A—D and A′—D′.

Discussion

Effects of the Structural Characteristics on the Charge Distribution at the Ring Carbons.—The nature of the extranuclear substituent is the main factor affecting the chemical shift. In line with previous observations on pyrimidines[7–9] and other structurally related compounds[10] with an analogous substitution pattern, the mean shielding at the ring carbons was observed to increase in the order =S < –SMe < –OMe < =O. In order correctly to appreciate the relative effects of these extranuclear substituents it is useful to observe that the centre of the full 42.4 p.p.m. range lies approximately at the

Table 1. The trimethyl-cyanurates and -thiocyanurates and their carbon-13 chemical shifts

Compounds					^{13}C Chemical shifts*								
					Ring carbons			*X*-Methyl carbons			*N*-Methyl carbons		
General formulae	X^2	X^4	X^6		C-2	C-4	C-6	X^2Me	X^4Me	X^6Me	N^1Me	N^3Me	N^5Me
M 	S	S	S	**(18)**	179.5	179.5	179.5	13.4	13.4	13.4			
	S	O	S	**(19)**	182.5	167.8	182.5	13.2	54.7	13.2			
	O	O	S	**(20)**	170.7	170.7	185.1	55.0	55.0	13.3			
	O	O	O	**(21)**	173.3	173.3	173.3	54.7	54.7	54.7			
N 	S	S	S	**(9)**	183.0	170.2	173.3		15.0	14.2		38.0	
	S	O	S	**(10)**	184.7	159.1	174.4		57.0	14.2		34.9	
	O	S	S	**(11)**	152.6	171.2	180.1		14.7	14.0		31.3	
	O	O	S	**(13)**	154.1	160.6	181.8		56.5	14.0		28.4	
	O	O	O	**(22)**	156.4	163.2	169.0		56.5	55.4		28.5	
	S	S	O	**(27)**[a]									
	S	O	O	**(28)**	187.4	162.2	164.2		57.1	56.1		35.0	
	O	S	O	**(29)**	155.7	174.6	167.6		14.7	55.5		31.4	
P 	S	S	S	**(1)**	175.5	162.4	180.5		15.3		43.3	38.7	
	S	O	S	**(2)**	176.1	151.5	183.4		57.4		43.7	36.4	
	S	S	O	**(3)**	177.0	169.2	149.2		15.7		36.6	38.1	
	S	O	O	**(5)**	178.7	158.1	152.0		57.0		36.2[b]	35.8[c]	
	O	S	O	**(14)**	150.0	170.0	152.5		15.0		28.8	31.8	
	O	O	O	**(16)**	150.7	159.0	154.0		56.7		29.1[b]	28.9[c]	
	O	S	S	**(24)**	147.5	164.1	183.6		15.1		35.4	31.6	
	O	O	S	**(25)**	148.8	153.6	185.8		57.3		35.6	29.6	
Q 	O	O	S	**(6)**	146.7	146.7	177.3				36.5	29.8	36.5
	O	O	O	**(17)**	148.0	148.0	148.0				29.0	29.0	29.0
	S	S	S	**(26)**	171.9	171.9	171.9				45.0	45.0	45.0
	S	O	S	**(23)**	175.1	145.0	175.1				44.6	37.0	37.0

* In p.p.m. from Me_4Si, in $CDCl_3$ solution. [a] Compound **(27)** has not been synthesized. [b] This signal could be assigned to the corresponding N^3Me carbons. [c] This signal could be assigned to the corresponding N^1Me carbon

same frequency of the carbon chemical shift of the common parent compound, the *s*-triazine (Figure 2), which is at 167.7 p.p.m.[11] This ordered distribution of signals makes it evident that the sulphur-containing substituents act as deshielding factors to the same extent as the corresponding oxygen-containing substituents act as shielding factors: in fact the centres of the corresponding ranges (C=S and C=O; C–SMe and C–OMe) lie at equivalent and opposite distances from it. According to the assumption of a linear relationship between the chemical shift and charge density, this is interpreted as sulphur being more effective than oxygen in subtracting π-electrons because of the availability of low energy *d*-atomic orbitals, in spite of its lower electronegativity.

The important role played by the valence states of the two nitrogen atoms in determining the chemical shift of the ring carbon between them is evident from the remarkable width of the four ranges. It is known that the polarity of C–N bonds, which affect the carbon shielding,[12] may vary according to the valence states of the nitrogen atoms. The way this structural character operates is apparent from the regular trend in the distribution of the sub-ranges. As a general rule the upfield region (see Figure 2) of each range always contains the signals of carbons bound to the *maximum compatible* number of V_3 nitrogens: two for the C=X groups and one for the C–XMe groups. The opposite occurs with the maximum compatible number of V_2 nitrogens; their higher effectiveness, with respect to the V_3 nitrogens, in deshielding the adjacent carbon is a consequence of the fact these 'basic' nitrogens generally tend to withdraw π-electrons from the ring and hence particularly to reduce the charge density of neighbouring atoms which experience a proportionally reduced shielding.

The way the shielding at each carbon is affected by the *meta–para*-geometry (as defined in Table 2) is evident from Figure 2; each group A and A′ of chemical shifts moves downfield with respect to B and B′ in the respective sub-ranges, and so correspondingly do the groups C and C′ with respect to D and D′. In order to account for this observation it seems important to note that the structural character under examination largely contributes to the overall geometry of the molecular frameworks of the carbon sites A—D and A′—D′; therefore the analysis of the observed effects can be conveniently carried out by examining the influence of the complete molecular geometry and structure on the charge density, and hence on the chemical shifts of the ring carbons. The observed downfield shift of carbons at site A in respect to those at site B (at site A′ with respect to B′, *etc.*) can, in other words, be correctly accounted for in terms of specific structural properties of the respective molecular frameworks, rather than in terms of specific properties of the atomic grouping defined by the *meta–para*-geometry.

Along these lines, each carbon site was first assigned to the respective molecular geometry which can be M′, N′, P′, or Q′

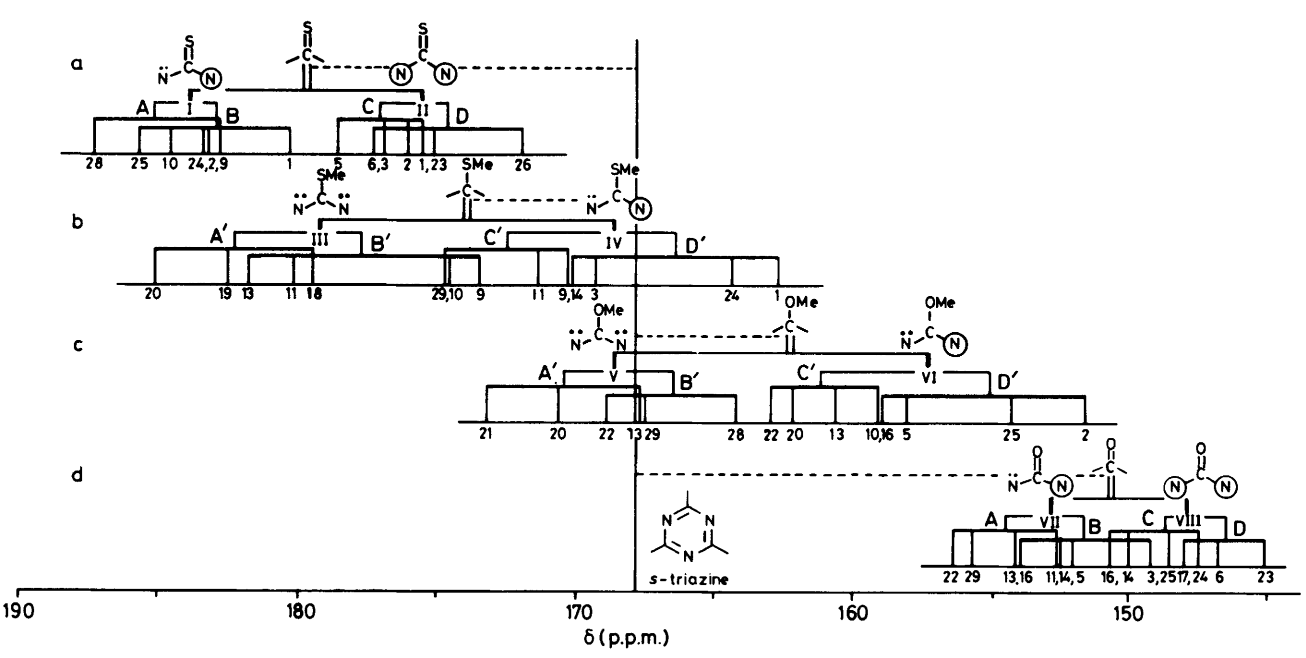


Figure 2. Assignment of the ring carbons peaks of the 23 compounds under examination following the classification procedure adopted. a, C=S range (15.5 p.p.m wide); its sub-ranges I (6.9) and II (6.9 p.p.m.); its groups A (4.4), B (5.2), C (3.1), and D (5.5 p.p.m.). b, C–SMe range (22.7 p.p.m wide); its sub-ranges III (11.8) and IV (12.2 p.p.m.); its groups A′ (5.7), B′(8.5), C′ (4.4), and D′ (7.6 p.p.m.). c, C–OMe range (21.8 p.p.m. wide); its sub-ranges V (9.1) and VI (11.7 p.p.m.); its groups A′(5.7), B′ (4.8), C′ (3.9), and D′ (7.4 p.p.m.). d, C=O range (11.4 p.p.m.); its sub-ranges VII (7.1) and VIII (5.7 p.p.m.); its groups A (3.7), B (4.7), 3 (3.3), and D (3.0 p.p.m.). · · · ·, Distances of the centres of the ranges from the *s*-triazine carbon peak: −12.0, −6.1, +5.3, and +17.0 p.p.m. for the ranges a—d respectively; centres of the 4 ranges (‖), 8 sub-ranges (❙), and 16 groups (|). The numbers at each peak bottom refer to the molecule (see Table 1) giving rise to that peak; according to their structure, molecules can generate one, two, or three ring carbons peaks; the same number can accordingly be found one, two, or three times, depending on the symmetry of the corresponding molecule

(corresponding to the general formulae M, N, P, and Q listed in Table 1):

Carbon sites	A	B	C	D	A′	B′	C′	D′
Molecular geometries	N′	P′	P′	Q′	M′	N′	N′	P′

Then, it was assumed that an adequate structural property for the present analysis was the π-electron delocalisation energy of the respective structures. This property, as measured by the π-energy gain, ΔE_π, was calculated in the frame of the Pariser–Parr–Pople approximation[13] for the eight compounds, among those under examination, which are listed in Table 3. These compounds, in which all the carbon sites and molecular geometries are represented, may be safely* taken as model compounds representative of the π-electron delocalisation of all the compounds under examination; therefore the mean value of the π-energy gain, $\overline{\Delta E_\pi}$ [obtained by averaging between the two calculated values relative to pairs of compounds with the same structure, *e.g.* (**18**) and (**21**), *etc.*] have been assigned to all the compounds with the same molecular geometry. These values, which appear much affected by the molecular geometries, may account for the observed trend of shielding and deshielding at ring carbon atoms: in fact, in each pair of carbon sites to be compared, one site systematically occurs in a different molecular geometry from the other and therefore experiences the effects of different delocalisation of the π-electron system. In particular, the downfield displacements of the chemical shifts of ring carbons A (A′) with respect to B (B′) and of C (C′) with respect to D (D′) are systematically related to the increased π-electron delocalisation, which brings in whatever the extranuclear substituent and the valence states of the adjacent nitrogen atoms, a decreased shielding at the ring carbons. This proves that the partition of the resonance peaks into groups, as described above (Figure 2), is not a peak classification artifact but is rooted in the overall electronic structure of the molecules under study.

A further correlation appears within each group depending on the nature of the hetero-atoms Z and Y in the *meta*-substituents. The four plots in Figure 3 show that the shielding at each C–R carbon in the groups A—D and A′—D′ increases linearly with the number of sulphur atoms (0, 1, or 2) in the *meta*-substituents.† As discussed above, the shielding effects of *meta*-sulphur atoms are related to their π-electron-withdrawing ability. The sulphur atoms in *meta*-substituents is operative on C–R ring carbons in competition with R, when R is =S or -SMe, whereas it operates in addition when R is =O or -OMe. The opposite occurs for the oxygen atoms in the *meta*-substituents.

Carbon Chemical Shifts and Charge Densities.—It has often been pointed out that a correlation may be expected between carbon chemical shifts and their charge densities. We therefore report the results obtained when both the π-charge and the total charge densities were considered for some model molecules

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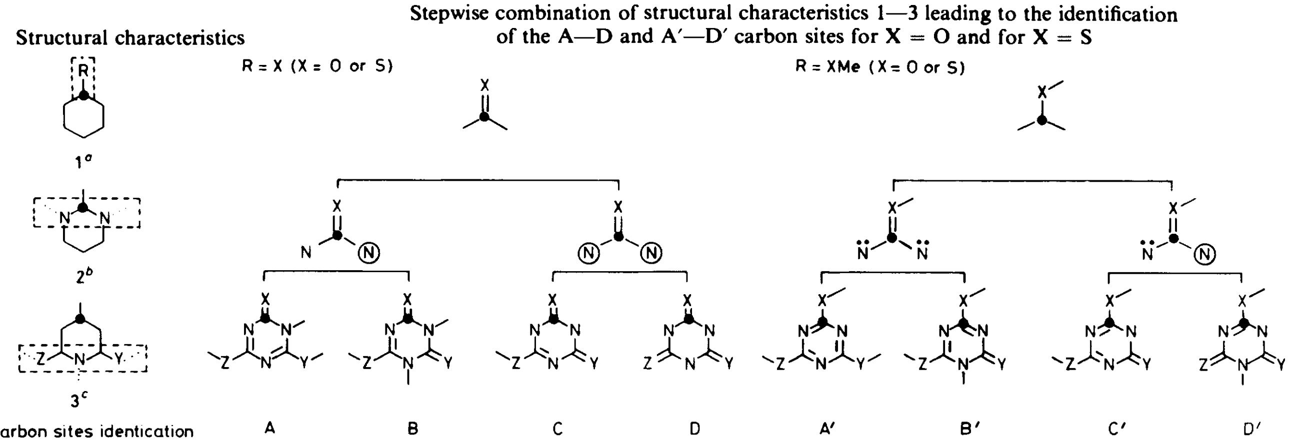
* These compounds are in fact the four trimethylcyanurates and the four trimethylthiocyanurates (the *OOO-* and the *SSS*-isomers listed in Table 1) whereas all the other compounds are *mixed OOS*-(monothiocyanurates) and *OSS*-(dithiocyanurates) derivatives of *s*-triazine: their ΔE_π values therefore reflect the extreme effects brought in by O–S substitution on the delocalisation energy. Furthermore their structures are distributed, two by two, among the four general formulae M, N, P, and Q (Table 1), they contain all the carbon sites examined, and their chemical shifts are so distributed to cover the whole 42.4 p.p.m. range.

† In the groups B and D an additional shielding effect is observed by the sulphur atoms in one of the two nonequivalent *meta*-positions due to the combined effects of their molecular site and valence states.

Table 2. Structural characteristics 1—3 considered for ring carbon classifications and their combination leading to the identification of 16 carbon sites A—D and A′—D′ (8 sites for X = O and 8 for X = S)



[a] Identity of the extranuclear substituent, R, bound to the considered ring carbon (●). [b] Valence states of the two adjacent nitrogen atoms. [c] Geometric arrangement of the *meta–para*-substitution; for the nature of the *meta*-sustituents Z and Y (Z, Y = O or S) and its influence on the chemical shift see Discussion section.

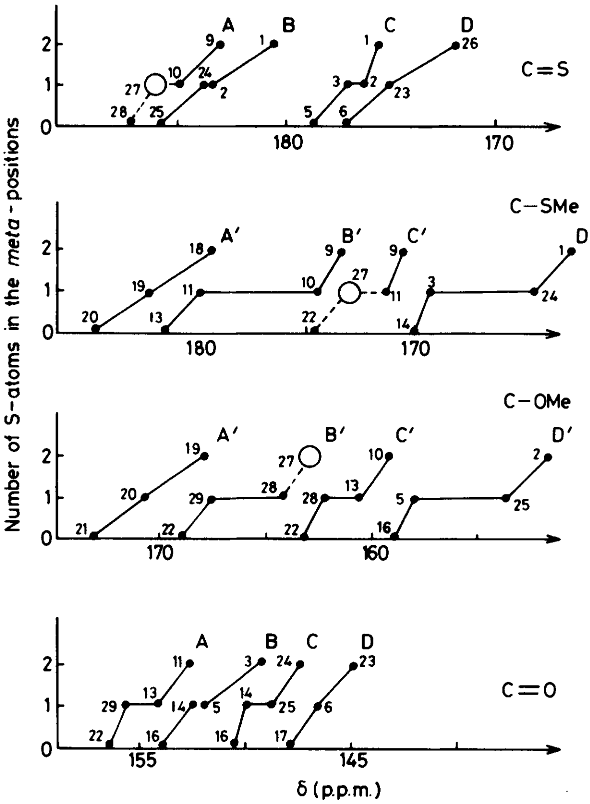


Figure 3. ^{13}C Chemical shifts (p.p.m. from Me_4Si) of ring carbons in each of the 16 groups reported as a function of the number (0, 1, 2) of sulphur atoms in the two *meta*-substituents. ○ Predicted chemical shifts values of the unknown compound of the series (**27**) (see Table 4)

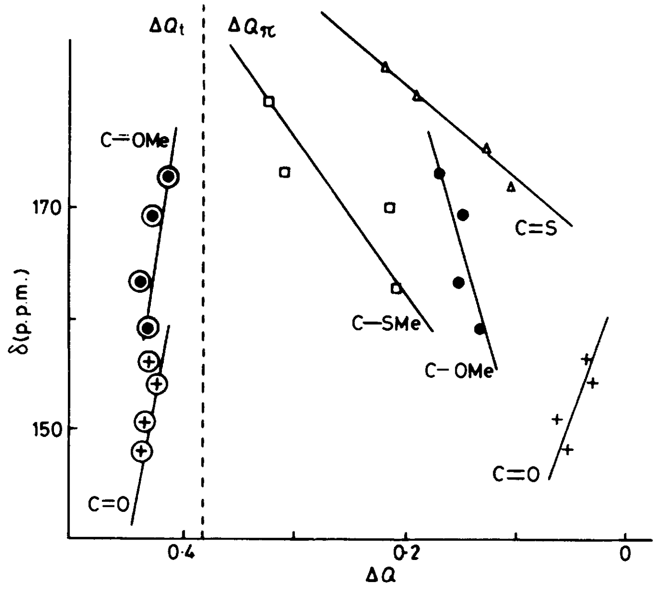


Figure 4. Observed ^{13}C chemical shifts of the C=S carbons of (**9**), (**1**), and (**26**). (△) C–SMe carbons of (**1**), (**9**), and (**18**); (□) C=O carbons of (**16**), (**17**), and (**22**); (+) C–OMe carbons of (**16**), (**21**), and (**22**); (●) plotted against the carbons π-charges, ΔQ_π. The chemical shifts of the C=O (⊕) and C–OMe (⊙) carbons of the above mentioned compounds are also plotted against the total atomic charges ΔQ_t

among those under investigation. π-Charges were already available for the carbon atoms in the isomeric structures of cyanuric and trithiocyanuric acid[14] and they are plotted in Figure 4 as a function of the observed chemical shifts of the corresponding carbons in the trimethyl-cyanurates and -trithiocyanurates: the chemical shifts of the C=S carbons of (**9**), (**1**), and (**26**) (see Table 1), of the C–SMe carbons of (**1**), (**9**), and (**18**); of the C=O carbons of (**16**), (**17**), and (**22**); and of the C–OMe carbons of (**16**), (**21**), and (**22**). In the same diagram the comparison is also shown with total charge densities.* From

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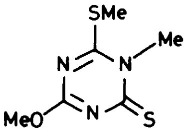
* They were obtained by means of the CNDO/2 full geometry optimisation procedure that only allowed the calculation of the theoretical parameters for the isomers of cyanuric acid; no convergence was observed for the sulphur-containing derivatives under the adopted calculation procedure.

Table 3. The eight compounds taken as models for the analysis of the effects of the π-electron delocalisation energy on the chemical shifts of carbons in site A *versus* site B, A′ *versus* B′ *etc.*; their π-energy gain, ΔE_π, and the π-energy gain mean values, $\overline{\Delta E}_\pi$, of pairs of compounds with the same molecular geometry

Model compounds		ΔE_π/eV				
(cyanurates)	(thiocyanurates)	cyanurates	thiocyanurates	$\overline{\Delta E}_\pi$/eV	Carbon sites present in model compounds	Molecular geometry
(21)	**(18)**	49.9	59.9	55	A′	M′
(22)	**(9)**	33.9	42.2	38	B′ C′ A	N′
(16)	**(1)**	18.7	21.3	20	D′ B C	P′
(17)	**(26)**	0	0	0	D	Q′

Table 4. Evaluation of the chemical shifts of the unknown compound (**27**)

Carbon	Subject	Predicted chemical shift
C=S	A	186.0 ± 0.5
C–SMe	C′	173.0 ± 0.5
C–OMe	B′	163.0 ± 0.5



(27)

Figure 4 it is evident that the chemical shifts correlate fairly well with the π-charges as previously reported.[5,6,8] The increase of π-charge lends to, as a rule, an increased shielding. We find however that the opposite occurs for the C=O peaks in our compounds: this shows that a simple correlation between π-charges and shielding effects may be inadequate when a number of competing effects operate in the same molecule. No apparent correlation was found with total charges (Figure 4).

Chemical Shifts and Reactivities.—Only a qualitative correlation can be made at the present stage of work between the C–SMe and C–OMe carbons reactivities and their chemical shifts. With respect to the thermal isomerisation of the C–OMe compounds, if the temperature range for the onset of reaction is taken as a relative reactivity index, the 12 compounds are distributed into four reactivity classes according to the following scheme:

OMe compounds	Isomerisation (Figure 1b)	Onset temp. range (°C)	Corresponding C–OMe sites
(2), **(25)**	(i-2)	0—10	D′, D′
(10), **(28)**	(i-2)	20—30	C′, C′
(5), **(16)**, **(13)**, **(22)**	(i-1)	80—100	D′, D′, C′, C′
(29), **(19)**, **(22)**, **(21)**	(i-1)	180—200	B′, A′, A′, A′

For the methanolysis of the C–SMe compounds, if the approximate methoxide anion concentration, relative to the substrate concentration, required for the methanolysis reactions to progress with comparable rates is taken as the reactivity index, the examined compounds are also distributed into four reactivity classes according to the following scheme:

SMe compounds	[OMe⁻]/[S]	Corresponding C–SMe sites
(1), **(24)**	0.01—0.02	D′, D′
(3), **(14)**, **(9)**, **(11)**	0.05—0.1	D′, D′, C′, C′
(10)	0.2—0.3	B′
(18), **(19)**, **(20)**	1—2	A′, A′, A′

In both cases it is apparent that compounds having C′ or D′ sites react much easier than those having A′ or B′ sites. A correlation of the reaction rates is under study and confirms the conclusion that the most shielded C–OMe and C–SMe sites react much faster than the deshielded sites.

Conclusions

The systematic procedure worked out allowed the identification of the structural characteristics responsible for the values of the ^{13}C chemical shifts and the evaluation of the extent of their effects; it has been shown that the observed shielding or deshielding effects can be qualitatively accounted for in terms of the modification that each structural character produced on the charge density at a given carbon. Such effects are in line with the Karplus–Pople theory which directly correlates higher shielding at a nucleus to higher charge density at that nucleus. These systematic effects produced on the chemical shifts of the C–R ring carbons (any one is R among the examined substituents) by the structural elements discussed, allow an easy prediction of the chemical shifts of the unknown compound (**27**). By applying the described procedure for classification of ring carbons and making use of the plots in Figure 3 it is possible to predict the interval (*ca.* 1 p.p.m. wide) where we expect that the resonance peaks of its three ring carbons fall. The results are shown in Table 4.

As for the correlation between chemical shifts and regioselectivity in the previously studied reactions[2] it has been shown that as a general rule, in both thermal rearrangements and solvolyses the more the carbons are shielded, the more they are reactive. It seems therefore possible to conclude that, within the set of compounds here considered, and perhaps in a wider sense, the ^{13}C chemical shift can be used as a reactivity index for thermal isomerisation and solvolysis reactions.

Experimental

Materials.—The compounds listed in Table 1 were synthesized as reported in refs. 1 and 2 and references cited therein.

N.m.r. Measurements.—Natural abundance PND ^{13}C n.m.r. spectra were obtained on a Varian XL 100 spectrometer at 25.16 MHz in the pulse Fourier transform mode. All spectra were recorded in $CDCl_3$ solutions (*ca.* 5×10^{-2}M; internal Me_4Si). Operating conditions were spectral width 5 000 Hz, probe temperature 32 °C, pulse width 15 μs, aquisition time 2 s, pulse delay 3 s, tube diameter 5 mm.

References

1 M. L. Tosato *J. Chem. Soc., Perkin Trans. 2*, 1979, 1371.
2 M. L. Tosato and L. Soccorsi, *J. Chem. Soc., Perkin Trans. 2*, 1982, 1321.
3 R. G. Shefers and J. L. Fedrik, *Adv. Heterocycl. Chem.*, 1965, **4**, 145.
4 M. Karplus and J. A. Pople, *J. Chem. Phys.*, 1963, **38**, 2803.
5 G. A. Olah and G. D. Matescu, *J. Am. Chem. Soc.*, 1970, **92**, 1430.
6 A. R. Tarpley and J. H. Goldstein, *J. Am. Chem. Soc.*, 1971, **93**, 3572.
7 J. S. Kwiatkowski and B. Pullman, *Adv. Heterocycl. Chem.*, 1975, **18**, 199 and literature cited therein.
8 I. W. G. Still, N. Plavac, D. M. MacKinnon, and M. S. Chauhan, *Can. J. Chem.*, 1978, **56**, 725.

9 G. W. H. Cheeseman, C. J. Turner, and D. J. Brown, *Org. Magn. Reson.*, 1979, **12**, 212.

10 R. Faure, E. J. Vincent, G. Assef, J. Kisler, and J. Metzger, *Org. Magn. Reson.*, 1977, **9**, 680.

11 P. C. Lauterbur, *J. Chem. Phys.*, 1965, **43**, 360.

12 J. B. Sothers in 'Carbon-13 NMR Spectroscopy,' eds. A. T. Blomquist and H. Wasserman, Academic Press, New York, 1972; W. F. Wehrli and T. Wirthlin in 'Interpretation of Carbon-13 N.m.r. Spectra,' Heyden, London, 1978.

13 M. Cignitti and L. Paoloni, *Theor. Chim. Acta*, 1967, **7**, 383.

14 L. Paoloni, M. Cignitti, and M. L. Tosato, Second Jerusalem Symposia on Quantum Chem. and Biochem., 1970, p. 324.

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