Guanidinium Trinitromethanide

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Guanidinium trinitromethanide monohydrate has been obtained from guanidinium chloride and either potassium trinitromethanide or iodotrinitromethane. An *ab initio* SCF-MO computational procedure (GAUSSIAN82) has been used to determine the optimized structures of guanidinium trinitromethanide and tricyanomethanide, the guanidinium cation, the trinitromethanide, tricyanomethanide, and cyanodinitromethanide anions. Electrostatic potentials have also been computed for the first two anions, as well as for the methanide anion.

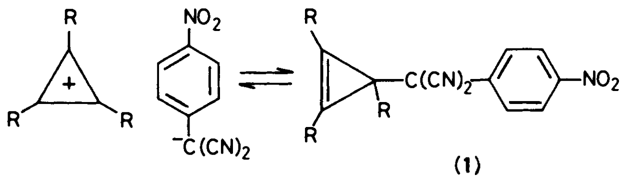
There is a developing interest in highly polar or ionic carbon–carbon bonds. Cyclopropenium *p*-nitrophenylmalononitriles (**1**) exist in the solid state as ionic compounds and in certain solutions as mixtures of ionic and covalent forms, equation (1).[1] The salt 2-nitropropan-2-ylbis-(*p*-methoxyphenyl)methylium trinitromethanide (**2**) has been described as being structurally incapable of existence in the covalent form, equation (2).[2] It is of interest that collapse of the salt (**2**) to a covalent nitronate ester, equation (3), was not detected. Presumably, the latter shares with many other alkyl nitronates a tendency to dissociate below 25 °C.[3]

Certain other trinitromethyl compounds coexist in equilibria between ionic and covalent carbon–nitrogen[4,5] and carbon–sulphur[6] bonds, equations (4) and (5).

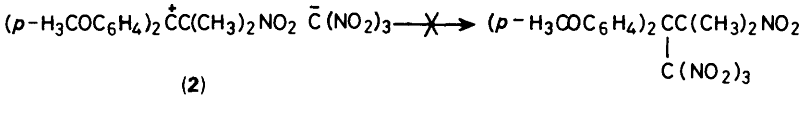
The low nucleophilicity that was implied for the trinitromethanide anion, equations (2), (4), and (5), is a characteristic shared with the tricyano-, and cyanodinitro-, and nitrodicyanomethanide anions insofar as it correlates with acid strengths[7] of nitroform [$HC(NO_2)_3$, pK_a 0], cyanoform [$HC(CN)_3$, pK_a -5], and cyanodinitromethane [$HC(NO_2)_2CN$, pK_a $-$ 6]. The presence of two of these electron-withdrawing substituents affords weaker acids (dinitromethane, pK_a 4 and dicyanomethane, pK_a 12),[7] and presumably somewhat greater nucleophilicities for the corresponding anions. The ability of the non-planar trinitromethanide anion to give an adduct with methyl acrylate under conditions whereby the planar dinitrocyanomethanide anion fails to react was attributed to more extensive *p*-electron delocalization in the latter.[7]

Iminium $[{>}N\overset{\cdots}{-}C{<}]^{+}$, amidinium $[{>}N\overset{\cdots}{-}\overset{|}{C}-N{<}]^{+}$, and guanidinium $[{>}N\overset{\cdots}{-}C(N{<})_2]^{+}$ cations offer both covalent (C–C) and ionic ($C^{+}C^{-}$) derivatives of nitro-, cyano-, and cyanonitro-methanide anions; however, documentation is sparse. In a report of a complex Michael reaction between a secondary amine and 1-nitro-2-phenylacrylonitrile an intermediate adduct, assumed to be a mixture of covalent and ionic isomeric forms, (**3a**) $\rightleftharpoons$ (**3b**), provided the anion of nitroacetonitrile that was needed in an explanation for the formation of the product (**4**), equation (6).[8a,b]

Alternatively the product from aminoguanidinium hydrogencarbonate and 1,1-dinitroethane is described as aminoguanidinium 1,1-trinitroethanide (**5a**) on the basis of ν(KBr)

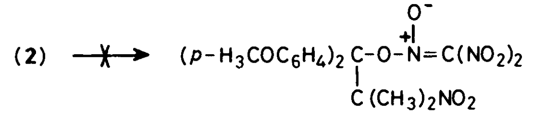


(1) (1)



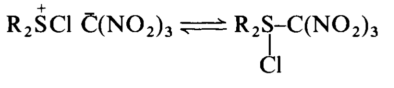
$$(p\text{-}H_3COC_6H_4)_2\overset{+}{C}C(CH_3)_2NO_2\ \overset{-}{C}(NO_2)_3 \not\longrightarrow (p\text{-}H_3COC_6H_4)_2\underset{\displaystyle C(NO_2)_3}{\underset{|}{C}}C(CH_3)_2NO_2 \qquad (2)$$

(2)

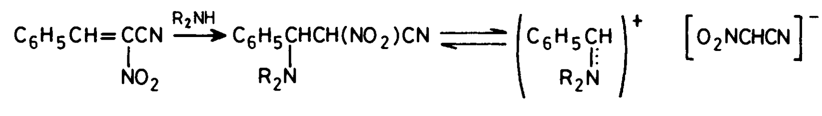


$$(\mathbf{2}) \not\longrightarrow (p\text{-}H_3COC_6H_4)_2\underset{\displaystyle C(CH_3)_2NO_2}{\underset{|}{C}}\text{-}O\text{-}\overset{\displaystyle O^-}{\overset{+|}{N}}{=}C(NO_2)_2 \qquad (3)$$

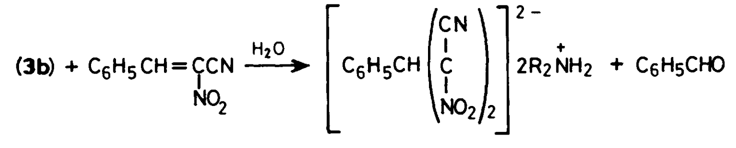
$$Ar\overset{+}{N}{\equiv}N\ \overset{-}{C}(NO_2)_3 \rightleftharpoons ArN{=}N\text{-}C(NO_2)_3 \qquad (4)$$



$$R_2\overset{+}{S}Cl\ \overset{-}{C}(NO_2)_3 \rightleftharpoons R_2\underset{\displaystyle Cl}{\underset{|}{S}}\text{-}C(NO_2)_3 \qquad (5)$$



(3a) **(3b)**



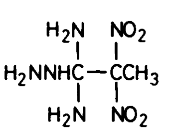
(4)

(6)

1 664 cm^{-1} ascribed to the cationic azomethide bond (C=N$^+$).[8c] The evidence did not exclude the coexistence of the covalent isomer (**5b**).

$H_2NNH\overset{+}{C}(NH_2)_2\ CH_2\overset{-}{C}(NO_2)_2$

(5a)



(5b)

Neither amidinium nor guanidinium trinitromethanides (**6**) and (**7**) and tricyanomethanides (**8**) and (**9**) have been reported; however, they appear to be readily available as derivatives of amidines [RC(=NH)NH$_2$, pK_a *ca.* 12] and guanidine [HN=C(NH$_2$)$_2$, pK_a 13].[9] To help resolve the question of the coexistence of each salt (**6**)–(**9**) with its C–C covalent counterpart (**10**)–(**13**), the preparation and characterization of guanidinium trinitromethanide (**7**) and/or its covalent form (**11**) were undertaken in conjunction with theoretical treatments of compounds (**11**) and (**13**), the guanidinium cation, and the trinitromethanide, tricyanomethanide, and the cyanodinitromethanide anions.

$Y\overset{+}{C}(NH_2)_2\overset{-}{C}Z_3$	$Y(H_2N)_2CCZ_3$
(**6**) $Y = H, Z = NO_2$	(**10**) $Y = H, Z = NO_2$
(**7**) $Y = NH_2, Z = NO_2$	(**11**) $Y = NH_2, Z = NO_2$
(**8**) $Y = H, Z = CN$	(**12**) $Y = H, Z = CN$
(**9**) $Y = NH_2, Z = CN$	(**13**) $Y = NH_2, Z = CN$

Discussion

Theoretical Analysis.—ab initio self-consistent-field molecular-orbital calculations were carried out with the GAUSSIAN82 procedure[10] for compounds (**11**) and (**13**) (taken to have C_3 symmetry), as well as for the carbocation (**14**) and the carbanions (**15**)–(**17**). All structures were optimized at the 3-21G level, which is known to be effective for this purpose.[11] As a guide to the distribution of charge in the ions (**14**)–(**17**), their electrostatic potentials were also computed; this is the potential $V(\boldsymbol{r})$ at each point in the space around a molecule due to its nuclei and electrons. $V(\boldsymbol{r})$ is given rigorously by equation (7):

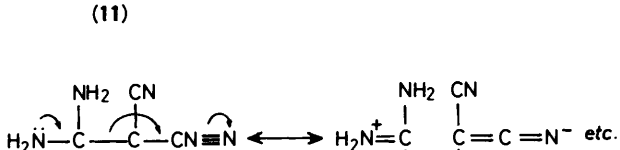
$\overset{+}{C}(NH_2)_3$	$\overset{-}{C}Y_2Z$
(**14**)	(**15**) $Y = NO_2, Z = NO_2$
	(**16**) $Y = CN, Z = CN$
	(**17**) $Y = NO_2, Z = CN$

$$V(\boldsymbol{r}) = \sum_A \frac{z_A}{|\boldsymbol{R}_A - \boldsymbol{r}|} - \int \frac{\rho(\boldsymbol{r}')d\boldsymbol{r}'}{|\boldsymbol{r}' - \boldsymbol{r}|} \quad (7)$$

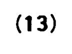
z_A is the charge on nucleus A, located at $\boldsymbol{R}_A$; $\rho(\boldsymbol{r})$ is the electronic density, which we obtained from the molecular wave function. The first term on the right side of equation (8) represents the potential due to the nuclei, while the second brings in the contribution of the electrons. Thus $V(\boldsymbol{r})$ is negative in those regions of space in which the effect of the electrons is dominant. The electrostatic potential is a well-established means for predicting and interpreting molecular reactive behaviour, especially toward electrophiles,[12–14] an important feature is that it is a real physical property, and can be determined experimentally (by diffraction methods) as well as computationally.[14]

Firstly, the structures of the ions (Table) are fully consistent with the resonance forms shown below, (**14**)–(**17**) in which the net charges are delocalized over the entire systems. The C–X bond lengths (X = NH$_2$, NO$_2$, or CN) are in each case considerably shorter than the typical values for C–N or C–C single bonds (1.47 and 1.53 Å, respectively[15]), indicating a significant degree of double-bond character. The bonds around the central carbons are coplanar, as are those within each NO$_2$ or NH$_2$ group; however, these groups are rotated to varying extents, presumably by steric effects.

When these ions are brought together to form (**11**) or (**13**), the bonds around the central carbons become roughly tetrahedral and the C–X distances increase markedly (Table). A particularly interesting feature of both (**11**) and (**13**) is the length of the central C–C bond, 1.60 Å, which is significantly longer than the typical 1.53 Å.[15] This suggests contributions from the ionic structures:



(11)

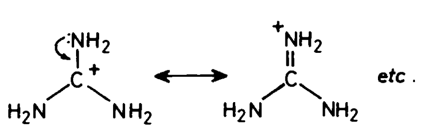


(13)

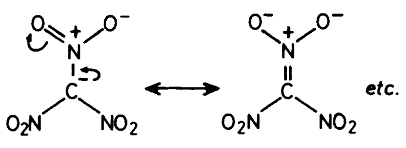
Table. Calculated structures.

Molecule	3-21G Energy/hartree	Distance/Å	Angle/°
$\overset{+}{C}(NH_2)_3$ **(14)**	−203.4011	C–N 1.324 N H 0.999	N–C–N 120 C–N–H 122 H–N–H 116 Dihedral angles[a] 89, 89, 90
$\overset{-}{C}(NO_2)_3$ **(15)**	−646.2672	C–N 1.383–1.393 N–O 1.256–1.262	C–N–O 118, 119 N–C–N 119–121 O–N–O 123 Dihedral angles[a] 63, 65, 67
$\overset{-}{C}(CN)_3$ **(16)**	−313.0768	C–C 1.400 C–N 1.150	C–C–N 180 C–C–C 120
$\overset{-}{C}(NO_2)_2CN$ **(17)**	−535.2265	C_c–NO_2[b] 1.372 C_c–C 1.399 C–N 1.142 N–O 1.256, 1.283	C_c–N–O[b] 116, 122 N–C_cN 125 O–N–O 122 C_c–C–N 180 C–C_c–N 118 Dihedral angles[a] 90, 90
$(H_2N)_3C$–$C(NO_2)_3$ **(11)**	−849.7622	C–C 1.602 C–NH_2 1.428 C–NO_2 1.493 N–H 0.997 N–O 1.229, 1.236	C–C–NH_2 106 H_2N–C–NH_2 113 C–N–H 117, 118 H–N–H 119 C–C–NO_2 112 O_2N–C–NO_2 107 C–N–O 116, 117 O–N–O 127
$(H_2N)_3C$–$C(CN)_3$ **(13)**	−516.5786	C–C 1.597 C–NH_2 1.440 C–CN 1.462 N–H 0.999, 1.001 C–N 1.137	C–C–NH_2 106 H_2N–C–NH_2 112 C–N–H 116, 117 H–N–H 116 C–C–CN 109 NC–C–CN 110 C–C–N 179

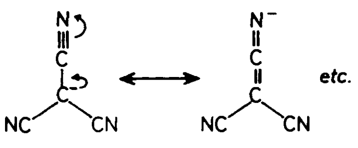
[a] The dihedral angles are between the planes of the NH_2 or NO_2 groups and the planes of the central portions of the ions. [b] The central carbon is indicated by the subscript *c*.



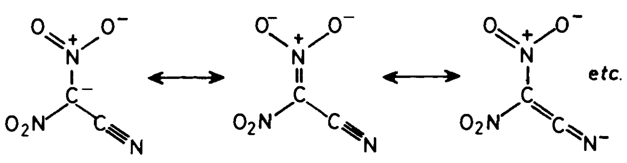
(14)



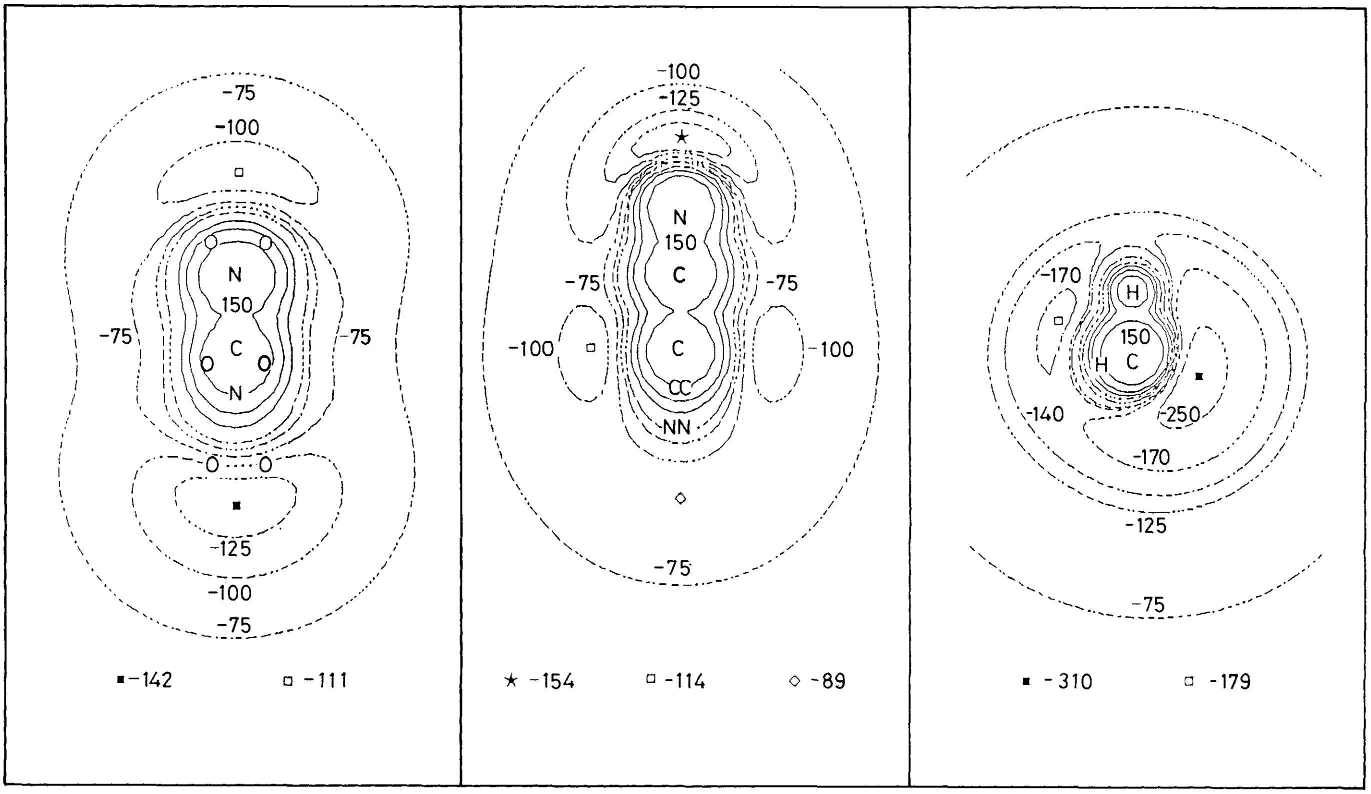
(15)



(16)



(17)



(a) (b) (c)

Figure. Calculated electrostatic potentials of $\bar{C}(NO_2)_3$ (*a*), $\bar{C}(CN)_3$ (*b*), and $\bar{C}H_3$ (*c*), in kcal mol^{-1}. Each potential is shown in a plane passing through the central carbon and one of the attached groups, and bisecting the angle between the other two groups. The positions, or projected positions, of all the nuclei are shown. Dashed contours correspond to negative values. The locations of the most negative potentials in this plane are indicated, and the magnitudes are given below each plot.

[The C–NO_2 distances in (**11**) indicate an absence of conjugation between the carbon and the nitro groups.] The long central C–C bonds that our calculations predict for (**11**) and (**13**) are fully consistent with the crystallographic finding that the analogous C–C bond in (**1**) (R = CH_3) has a length of 1.588 Å.[1a] It should also be noted that there is clear evidence of intramolecular hydrogen bonding in (**11**); each nitro group has an oxygen that is 2.21 Å from an amino hydrogen, which is considerably less than the sum of the oxygen and hydrogen van der Waals radii, 1.40 and 1.20 Å, respectively.[16]

The Figure shows the calculated electrostatic potentials of $\bar{C}(NO_2)_3$, $\bar{C}(CN)_3$, and the unsubstituted methanide ion, $\bar{C}H_3$.[17] As is normal for anions, each is completely surrounded by negative potential, which reaches its strongest points near the central carbon and also in the vicinities of the attached groups. The central carbon is most negative in the case of $\bar{C}H_3$ and least negative for $\bar{C}(NO_2)_3$, due to the presence of the very strongly electron-withdrawing nitro group. This trend is reflected in the calculated heterolysis energies of the C–C

$$(H_2N)_3C\text{–}C(NO_2)_3 \longrightarrow (H_2N)_3\overset{+}{C} + \bar{C}(NO_2)_3 \quad \Delta E = 59 \text{ kcal mol}^{-1} *$$

$$(H_2N)_3C\text{–}C(CN)_3 \longrightarrow (H_2N)_3\overset{+}{C} + \bar{C}(NO_2)_3 \quad \Delta E = 63 \text{ kcal mol}^{-1}$$

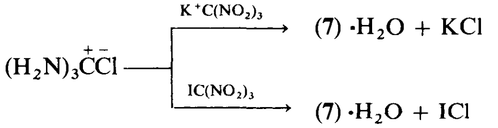
bonds in (**11**) and (**13**), compared with that of ethane:[17]

$$H_3C\text{–}CH_3 \longrightarrow \overset{+}{C}H_3 + \bar{C}H_3 \quad \Delta E = 342 \text{ kcal mol}^{-1}$$

That the anion $\bar{C}(CN)_3$ has a more negative electrostatic potential than $\bar{C}(NO_2)_3$ indicates the former to be more nucleophilic, consistent with the pK_a values cited earlier for $HC(CN)_3$ and $HC(NO_2)_3$.

Results

Preparation and Characterization.—Upon being mixed in methanol, guanidinium chloride and potassium trinitromethanide gave guanidinium trinitromethanide (**7**) monohydrate as a bright-yellow crystalline solid, equation (8). It was also obtained from guanidinium chloride and iodotrinitromethane, equation (8). However, tetranitromethane and guanidinium chloride did not interact and were recovered.



$$(H_2N)_3\overset{+}{C}\overset{-}{Cl} \begin{cases} \xrightarrow{K^+\bar{C}(NO_2)_3} (7)\cdot H_2O + KCl \\ \xrightarrow{IC(NO_2)_3} (7)\cdot H_2O + ICl \end{cases} \qquad (8)$$

Storage of the hydrated salt (**7**) for several days at 25 °C or under refrigeration (10 °C) brought about a decomposition with loss of colour that precluded satisfactory elemental analysis. Thermolysis of a neat sample brought about gas evolution at 110–120 °C and produced a colourless amorphous unidentified solid $(C_2H_{10}N_8O_{12})_n$. The yellow salt, ammonium trinitromethanide,[18] $CH_4N_4O_6$, was an expected product, but was not detected. The structure of the salt (**7**) monohydrate was confirmed by an *X*-ray crystallographic analysis. Attempts to obtain the anhydrous salt (**7**) were unsuccessful.

On storage at 25 °C in ethyl acetate the hydrated salt (**7**) (10^{-4} mol dm^{-3}) showed an initial λ_{max} 350 nm (ε 15 000) [$\bar{C}(NO_2)_3$]

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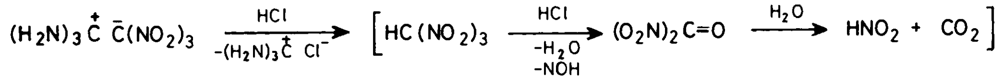
* 1 cal = 4.184 J.



$$(H_2N)_3\overset{+}{C}\ \overset{-}{C}(NO_2)_3 \xrightarrow[-(H_2N)_3\overset{+}{C}\ Cl^-]{HCl} \left[HC(NO_2)_3 \xrightarrow[\substack{-H_2O\\-NOH}]{HCl} (O_2N)_2C{=}O \xrightarrow{H_2O} HNO_2 + CO_2\right]$$

(7)

(9)

that gradually diminished over 5 days to ε 10 500 with no further change on storage for an additional 5 days. Removal of the solvent after 10 days gave a quantitative recovery of the hydrated salt (7), identified by (KBr) comparison of the i.r. spectroscopic data with those of an authentic sample. An ethyl acetate solution of the recovered salt showed λ_{max} 350 (ε 10 500) that did not change on storage. A similar loss in molar absorption coefficient and recovery of the hydrated salt (7) in acetonitrile was observed.

Fragments detected in the mass spectrum of the salt (7) monohydrate (*M* 228) revealed dehydration and the incremental loss of the elements of nitramine H_2NNO_2(*M*62) to give *m*/*z* 149 $(C_2H_5B_2O_4)^+$ that was assigned to protonated 1,1-diamino-2,2-dinitroethene $(O_2N)_2C{=}C(NH_2)_2{\cdot}H^+$, or tautomer, and *m*/*z* 87 $(C_2H_3N_2O_2)^+$ that was assigned to protonated aminonitroacetylene $O_2NC{\equiv}CNH_2{\cdot}H^+$ or tautomer. Fragments at *m*/*z* 59 $(CH_5N_3)^+$ and *m*/*z* 43 $(CH_3N_2)^+$ were presumably derived from guanidine in accordance with a previous report.[19]

The salt (7) was converted into guanidinium chloride by treatment with anhydrous hydrogen chloride according to equation (9). Presumably undetected nitroform was also produced and underwent fragmentation initiated by the Nef reaction, equation (9).

Guanidinium chloride readily reacted with potassium dinitromethanide, $KCH(NO_2)_2$, to give an unstable, crystalline, unidentified, yellow salt, $(C_2H_{11}N_5O_4)_n$. A similar reaction with potassium nitromethanide, KCH_2NO_2, and guanidinium chloride gave a dark intractable product that decomposed after being left to stand.

Experimental

Instruments used included a Pye Unicam SP 200 i.r., a Cary 17 u.v. spectrophotometer, and a Hewlett Packard 5985 g.c.–m.s. T.l.c. was carried out on analytical precoated silica gel plates (Eastman Kodak). Elemental analyses were obtained from Micro Tech Laboratories, Skokie, Illinois and Midwest Micro Lab., Indianapolis, Indiana. Guanidine hydrochloride was commercially available from Aldrich Chemical Company. The potassium salt of trinitromethane[20] and iodotrinitromethane[21] were prepared according to published procedures.

Guanidinium Trinitromethanide (7) *Hydrate*.—To a suspension of potassium trinitromethanide (1.5 g, 8 mmol) in methanol (25 cm^3) cooled to 0 °C, was added dropwise with stirring a solution of guanidinium chloride (0.77 g, 8 mmol) in methanol (20 cm^3). After the addition, the reaction was brought to room temperature and stirred for 3 h. Methanol was removed from the solution and the residue was supended in ethyl acetate (20 cm^3) and the insoluble potassium chloride (0.21 g, 74 %), was isolated. Ethyl acetate was removed from the filtrate and the residue was titrated with ether to give the hydrated compound (7) as a yellow solid, 0.64 g (76 %); m.p. 110–120 °C (decomp.) after recrystallization from a mixture of ethyl acetate and ether 60/40. It was shown to be homogenous by t.l.c. (silica gel, R_F 0.4, ethyl acetate); i.r. (KBr) 3 350br, 1 650 ($C{=}N^+$), 1 390, 1 260, and both 780 and 720 cm^{-1} $[(O_2N)_3C^-]$; λ_{max}(MeOH) 350 nm (ε 1.33×10^4) $[^-C(NO_2)_3]$; *m*/*z* (70 eV) 149 $(C_2H_5N_4O_4)^+$ (10%), 129 (10), 87 $(C_2H_3N_2O_2)^+$ (20), 70 $(C_2NO_2)^+$ (15), 59 $(CH_5N_3)^+$ (10), 57 (20), 46 (NO_2) (100), and 43 $(CH_3N_2)^+$ (60). The compound was recrystallized from acetone for *X*-ray structure determination. Satisfactory elemental analyses were precluded by slow decomposition at room temperature.

To a stirred solution of iodotrinitromethane (ITM) (0.16 g, 0.6 mmol) in methanol (5 cm^3) cooled to 0 °C, was added guanidine hydrochloride (0.11 g, 0.6 mmol) in methanol (5 cm^3). After the addition the solution was stirred at room temperature for 2 h. A similar work-up produced the hydrated salt (7), (0.045 g, 36%), m.p. 110–120 °C (decomp.) identified by its m.p. and comparison of its i.r. spectrum with that of an authentic sample.

A suspension of the hydrated salt (7) (0.23 g, 1 mmol) in ether (15 cm^3) was cooled to 0 °C with ice and acetone; anhydrous hydrogen chloride gas was slowly bubbled through the suspension until the yellow colour disappeared. Guanidine hydrochloride precipitated as a colourless crystalline solid (0.075 g, 78%), m.p. 180–182 °C after isolation and drying. It was identified by comparison with authetic data (lit.,[22] m.p. 186–188 °C).

Acknowledgements

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