

# Synthesis and structural analysis of some trinitromethanide salts

A.A. Gakh\*, J.C. Bryan, M.N. Burnett, P.V. Bonnesen

*Chemical and Analytical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6197, USA*

Received 23 April 1999; accepted 16 July 1999

## Abstract

Two trinitromethanide (TNM) salts containing weakly coordinating cations (tetrabutylammonium and cesium) were synthesized via incomplete nitration of acetic anhydride followed by cation exchange with tetrabutylammonium bromide and cesium fluoride. Their structural characteristics were determined by single crystal X-ray crystallography [J.C. Bryan, M.N. Burnett, A.A. Gakh, *Acta Crystallogr., Sect. C (Cr. Str. Comm.)* 54 (1998) 1229] followed by comparative analysis with the literature data. In all cases, the TNM anion was found to be a non-planar system. The sum of dihedral angles between the central (C–N<sub>3</sub>) plane of the anion and the planes of the individual nitro groups varies from 60 to 100°. C–N and N–O interatomic distances in TNM anion can be correlated with the dihedral angles of the corresponding nitro groups. The <sup>13</sup>C and <sup>14</sup>N NMR spectra of the TNM anion are very simple (broad singlets), an indication of the equivalence (on the NMR time scale) of the nitro groups in solution. The distribution ratio between organic phase (tributyl phosphate) and water is 5000 times higher for Cs<sup>+</sup>C(NO<sub>2</sub>)<sub>3</sub><sup>−</sup> compared to Cs<sup>+</sup>NO<sub>3</sub><sup>−</sup>, presumably due to size and/or charge delocalization differences between nitrate and TNM anions. © 2000 Elsevier Science B.V. All rights reserved.

**Keywords:** Trinitromethane; Y-conjugation; Nitration; X-ray crystallography; NMR; Dendritic anions

## 1. Introduction

Simple Y-conjugated [1–5] anions (such as nitrate ion) occupy a special place in chemistry due to their important roles in natural and industrial chemical processes. Another classic example of Y-conjugated anions is trinitromethanide (TNM) anion (**II**, Scheme 1—a family of Y-conjugated anions). More complex structures (such as **III**) can also be envisioned.

The nitrate ion (**I**, Scheme 1) is planar due to the energy benefits of Y-delocalization [1,3] that is maximized for planar structures. “Dendritic” anions **II** and **III** (e.g., TNM or unreported hexanitroisobutylene dianion) are not planar systems due to steric and elec-

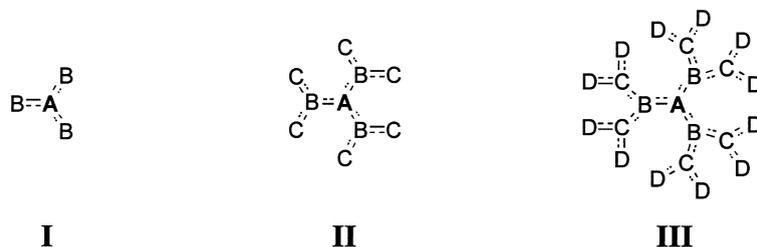
trostatic interactions between the terminal oxygen atoms [3]. The interplay of factors affecting the geometry of TNM anion is complex and was the subject of several publications [6–10]. This article is devoted to the synthesis and structural analysis of two trinitromethane salts with weakly coordinating cations, tetrabutylammonium and cesium.

## 2. Results and discussion

Trinitromethane and its salts have been known for almost 100 years [11,12]. Existing physical–chemical data include results of ab initio calculations [7–10] and single crystal X-ray crystallographic studies [13–21]. We studied two TNM salts containing weakly coordinating cations, tetrabutylammonium and cesium. The synthesis of these salts was based

\* Corresponding author. Tel.: + 1-202-586-6562; fax: + 1-202-586-2164.

E-mail address: gakhaa@ornl.gov (A.A. Gakh).



Scheme 1.

on previously reported procedures (such as nitration of acetic anhydride (Scheme 2—synthesis of tetrabutylammonium salt of trinitromethane [22]) modified to achieve better results (see Experimental).

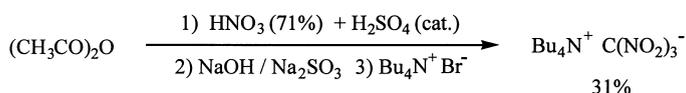
Both tetrabutylammonium and cesium salts of trinitromethane are bright-yellow solids which can be recrystallized from water or water–methanol mixtures. ORTEP [23,24] drawings (performed using ORTEP-3 for Windows) of TNM anion in cesium and tetrabutylammonium salts are presented in Fig. 1 and Fig. 2, respectively [25].

Analysis of the literature data [13–21] indicates that the TNM anion in various salts retains some common structural features. Thus, the central plane C–N<sub>3</sub>, (A–B<sub>3</sub> in **II**, Scheme 1) is preserved, as well as the planes of the individual nitro groups C–NO<sub>2</sub>, (A–BC<sub>2</sub> in **II**, Scheme 1). However, the dihedral angles between the major C–N<sub>3</sub> plane and the planes of the individual nitro groups vary from one structure to another. Typical conformations of the TNM anion contain two nitro groups almost coplanar (dihedral angles 3–8°) with the C–N<sub>3</sub> plane, and one nitro group out-of-plane at a substantial angle. However, there are several reported examples of TNM salts in which all three nitro groups are twisted in a propeller-like manner with respect to the central plane of the molecule. It is worth mentioning here that ab initio calculations give preference to propeller-like (D<sub>3</sub>) structures with dihedral angles between the planes of the nitro groups and the central plane of the anion ranging from 27.5 [7] to 67° [6].

The sums of the dihedral angles between the central plane of the anion and the planes of nitro groups vary from one structure to another in a range of 60–100° [13–21]. The non-planar character puts some limitations on the extent of involvement of Y-conjugation for this anion, which is reflected in several physical–chemical features. For example, the p*K*<sub>a</sub> value of the corresponding acid (trinitromethane) is much higher (p*K*<sub>a</sub> = 0) than expected by comparison with related planar systems (such as cyanodinitromethane, p*K*<sub>a</sub> = –6) [6].

Similarities in the known conformations of the TNM anion allow us to analyze the relationships between the geometrical characteristics of the nitro groups (such as C–N and N–O distances) and dihedral angles between the C–N<sub>3</sub> plane of the molecule and planes of these nitro groups. The results of this compilation are presented in Fig. 3. The analysis shows that there is a correlation between the length of the C–N and N–O bonds and the corresponding dihedral angles, as expected. Thus, C–N bonds are longer in out-of-plane nitro groups and shorter in in-plane nitro groups. There is also a reverse tendency for N–O distances.

These observations are in line with the expected effects of delocalization of negative charge in these anions. Delocalization is most effective for the in-plane nitro groups and decreases with increasing dihedral angle. This delocalization leads to shorter C–N distances and longer N–O distances, as observed. It is worth mentioning that in trinitromethane, HC(NO<sub>2</sub>)<sub>3</sub>, the C–N distances are 1.50–1.51 Å and the N–O



Scheme 2.

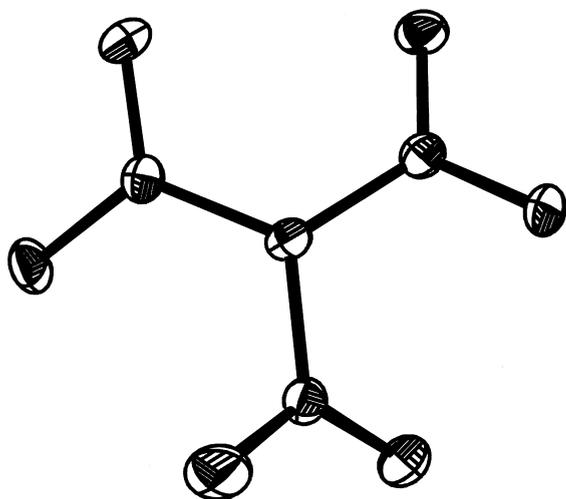


Fig. 1. ORTEP drawing of TNM anion in  $\text{Cs}^+$  salt (50% thermal ellipsoids).

distances are 1.20–1.21 Å [26]. The observed C–N distances (1.35–1.45 Å) in TNM anions are slightly shorter than in trinitromethane itself. This effect of ionization on the structural characteristics of trinitromethane can be attributed to the differences in the hybridization of the central carbon atom ( $\text{sp}^3$  in trinitromethane and  $\text{sp}^2$  in TNM anion). Suggested Y-aromatic character of TNM anion [7] could also be a contributing factor, affecting the above mentioned geometrical features.

The structural characteristics (bond distances and

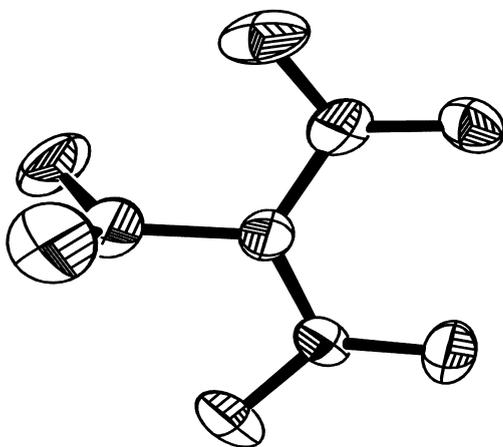


Fig. 2. ORTEP drawing of TNM anion in  $\text{Bu}_4\text{N}^+$  salt (50% thermal ellipsoids).

dihedral angles) of tetrabutylammonium and cesium salts of trinitromethane are presented in Table 1. They fall within the corridor of expected values (Fig. 4). This observation indicates that in tetrabutylammonium and cesium salts the TNM anion has typical structural parameters. However, the conformations of the anion in these two salts are different. The TNM anion in the tetrabutylammonium salt has two in-plane nitro groups (dihedral angles close to  $0^\circ$ ). The third nitro group is twisted with a dihedral angle of  $86^\circ$ . As we mentioned earlier, this conformation is very common for the TNM anion. In contrast, the TNM anion in the cesium salt belongs to the rare group of conformations in which all three nitro groups are more evenly twisted relative to the central plane. The sums of the dihedral angles of the nitro groups versus the central plane are  $73^\circ$  for the tetrabutylammonium salt and  $92^\circ$  for the cesium salt.

An investigation of the TNM anion in solution was performed using  $^{14}\text{N}$  and  $^{13}\text{C}$  NMR spectroscopy. The  $^{14}\text{N}$  spectrum of the anion (tetrabutylammonium salt in acetone- $\text{D}_6$ ) was very simple: one line (line width  $< 20$  Hz) at room temperature. The  $^{13}\text{C}$  NMR spectrum of the anion (tetrabutylammonium salt in acetone- $\text{D}_6$ ) also has one broad signal (line width  $\geq 10$  Hz) at 151.6 ppm. The  $^{13}\text{C}$  spectrum of the cesium salt in  $\text{DMSO-}d_6$  was very similar and consisted of one broad signal at 150.3 ppm. Line broadening in the  $^{13}\text{C}$  spectra could be attributed to  $^{13}\text{C}$ – $^{14}\text{N}$  spin interactions known for such systems [27,28]. No dynamic exchange processes were detected for salts of trinitromethane using variable-temperature NMR [29]. Apparently, the barrier of rotation of three nitro groups in this anion is too small to be detected by this method, or the anion assumes an average symmetrical conformation in solution. Similar conclusions have been drawn based on solution NMR [30] and solid state IR [31] data.

Finally, the results of the structural analysis allow us to suggest that salts of trinitromethane (**II**, Scheme 1) can be extracted into an organic phase from water solutions much easier than nitrate salts (**I**, Scheme 1) due to its larger size. The results of extraction experiments are presented in Table 2. The data show that the TNM anion indeed facilitates the extraction of cesium from water solutions. The distribution ratio of cesium TNM is almost 5000 times higher than cesium nitrate in a tributyl phosphate/water (TBP/ $\text{H}_2\text{O}$ ) system

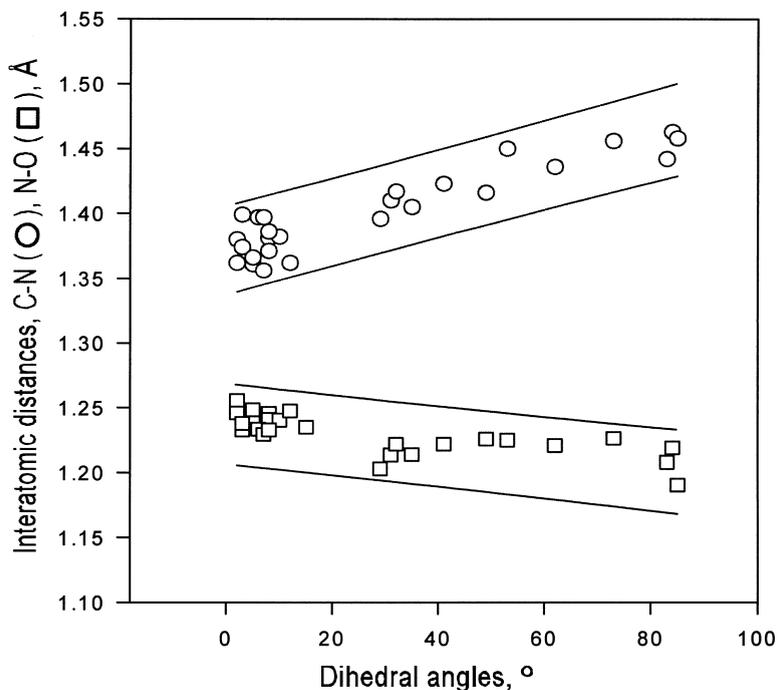


Fig. 3. Distribution of bond lengths (C–N, open circles; and N–O, open squares) versus dihedral angles of individual nitro groups in various salts of trinitromethane (literature data).

(Table 2). This difference reflects the anion size discrimination in the extraction process [32].

It is also worth mentioning here that these two anions are also different in relation to the effects of additives. Thus, the addition of 2,2,3,3,4,4,5,5-octafluoropentane-1-ol (OFP) (a potent hydrogen bond donor) to TBP/H<sub>2</sub>O mixtures slightly improves the extraction of cesium nitrate, but it has negative impact on the extraction of cesium TNM.<sup>1</sup> A possible explanation is that the negative charge is more widely distributed in the TNM anion compared with the nitrate anion.<sup>2</sup> This in turn could lead to weaker

bonding since the energies of hydrogen bonds involving anions are affected by the distribution of negative charge in these anions [32,33].

### 3. Experimental

#### 3.1. General

Melting points are not corrected. All reagents and solvents were used as received (Aldrich, Baxter). Cesium-137 tracer was obtained as CsCl solution in 1 M HCl from Amersham. <sup>1</sup>H, <sup>13</sup>C and <sup>14</sup>N NMR spectra were recorded with a Bruker MSL spectrometer operating at 400.13 MHz (<sup>1</sup>H), 100.61 MHz (<sup>13</sup>C), and 28.91 MHz (<sup>14</sup>N). All chemical shifts are quoted in ppm relative to TMS (<sup>1</sup>H, <sup>13</sup>C) or Bu<sub>4</sub>N<sup>+</sup> Br<sup>-</sup> (<sup>14</sup>N). UV–VIS spectra were measured using a Cary UV–VIS spectrometer.  $\gamma$ -counting was performed using a Packard 5003 Cobra Quantum Counter with a 3'' NaI (Tl) crystal. Full details of X-ray experiments are published elsewhere [25].

<sup>1</sup> Relatively small effect of addition of OFP on the extraction process in TBP/H<sub>2</sub>O systems could be explained by taking into account the existence of strong hydrogen bonding between the organic solvent (TBP) and the alcohol (OFP) confirmed by <sup>1</sup>H NMR studies of the TBP/OFP mixtures (A.A. Gakh, unpublished results). This feature puts some limitation on the extent of anion hydrogen bonding in these systems due to the competition between the solvent and the anion for hydrogen bond donor.

<sup>2</sup> It is not very obvious but well documented that in TNM anion the negative charge resides predominantly on the oxygen atoms [8,9,30].

Table 1  
Selected structural parameters of TNM anion in the tetrabutylammonium and cesium salts of trinitromethane

Nitro group #	Tetrabutylammonium salt			Cesium salt		
	Dihedral angle (°)	C–N distance (Å)	Average N–O distance (Å)	Dihedral angle (°)	C–N distance (Å)	Average N–O distance (Å)
1	86	1.453	1.208	42	1.439	1.225
2	5	1.390	1.241	21	1.382	1.242
3	2	1.372	1.246	10	1.385	1.240

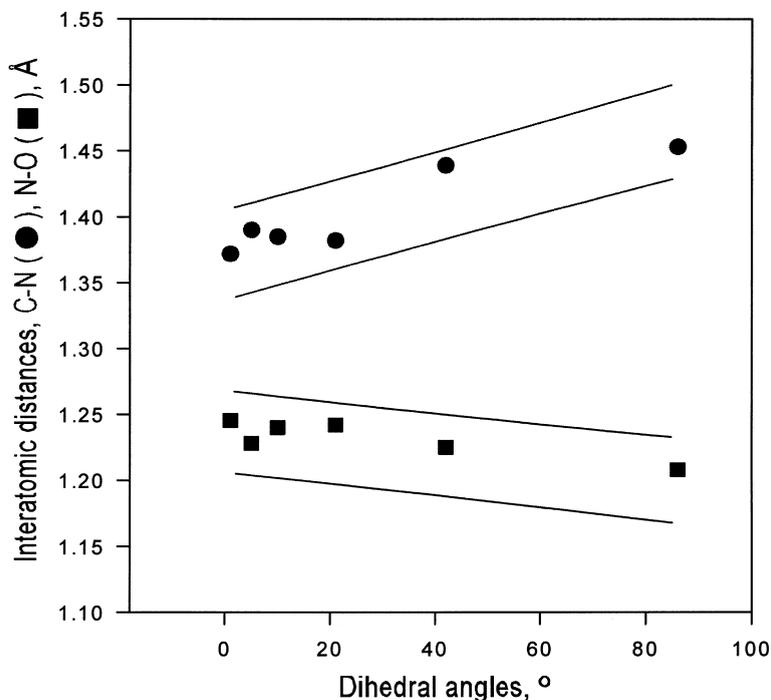


Fig. 4. Distribution of bond lengths (C–N, filled circles; and N–O, filled squares) versus dihedral angles of individual nitro groups in  $\text{Bu}_4\text{N}^+$ - and  $\text{Cs}^+$ - salts of trinitromethane.

### 3.2. Caution

Alkali salts of trinitromethane are sensitive explosives. Proper protective measures (shields, glasses) should be used during experiments with these materials. All measurements involving the radiotracers (Cs-137) should be performed in accordance with the appropriate procedures using certified equipment.

Table 2

Extraction results of cesium nitrate and cesium TNM in tributyl phosphate/water systems

Organic solvents	$D^a(\text{Cs}), \text{Cs}[\text{C}(\text{NO}_2)_3]$	$D^a(\text{Cs}), \text{CsNO}_3$
Neat TBP <sup>b</sup>	1.72	0.000352
OFP and TBP <sup>c</sup>	1.01	0.000375

<sup>a</sup> Distribution ratio  $D$ :  $C(\text{Cs})_{\text{org}}/C(\text{Cs})_{\text{water}}$ ;  $\pm 3\%$ .

<sup>b</sup> TBP, tributyl phosphate.

<sup>c</sup> 10 wt% (about 0.43 M) of 2,2,3,3,4,4,5,5-octafluoropentan-1-ol (OFP) in tributyl phosphate (TBP).

### 3.3. Tetrabutylammonium salt of trinitromethane

50.0 g of 71% ( $d = 1.42$ )  $\text{HNO}_3$  (0.56 mol of  $\text{HNO}_3$  and 0.81 mol of  $\text{H}_2\text{O}$ ) was added dropwise with stirring to 180 g (1.76 mol) of acetic anhydride. The temperature rose quickly to 35–40°C during the first few minutes of the addition and was maintained at this level using external cooling (ice-water). At the end of the addition, the exothermic reaction subsided, and the temperature was allowed to drop to 30–35°C. After the addition of nitric acid was completed, the reaction mixture was stirred at the same temperature (30–35°C) for an additional 5 min. Catalytic amounts of concentrated sulfuric acid (1.0 ml, 1.84 g, 18 mmol) were then added dropwise. The temperature of the reaction mixture was held at 30–35°C during the next 2 h by using cold water cooling and by adjusting the speed of stirring. During this time, the color of the reaction mixture turned brown ( $\text{NO}_x$ ) with slow evolution of gases. The stirring was stopped after 2 h, and the reaction mixture was allowed to stay at room temperature for an additional 2 days. The reaction

mixture was then partially neutralized using a solution of NaOH (60 g, 1.5 mol) and Na<sub>2</sub>SO<sub>3</sub> (20 g, 0.16 mol) in 500 ml of ice-water mixture. Most of the NO<sub>x</sub> was removed from the solution by air bubbling (20 min). Then a solution of tetrabutylammonium bromide (30 g, 0.14 mol in 100 ml of H<sub>2</sub>O) was added slowly with stirring at 5–10°C to allow crystallization of the yellow oil (tetrabutylammonium salt of trinitromethane). After crystallization was complete (3–5 h of stirring), the yellow precipitate was filtered off, washed several times with cold water, and air-dried. The compound was purified by precipitation from MeOH solution (water was slowly added to 250 ml of MeOH solution containing 25–30 g of crude salt at 0–5°C) to yield 22.3 g (57 mmol, 31%) of tetrabutylammonium salt of trinitromethane with m.p. 88–89°C (dec). Anal calcd. for C<sub>17</sub>H<sub>36</sub>N<sub>4</sub>O<sub>6</sub> C 52.02, H 9.24, N 14.27; found, C 52.58, H 9.42, N 13.91. UV–VIS: λ<sub>max</sub> = 350 nm; E = 14,600 (MeOH). <sup>1</sup>H NMR (acetone-D<sub>6</sub>): 0.97 m (12H, CH<sub>3</sub>), 1.42 m (8H, CH<sub>2</sub>), 1.77 m (8H, CH<sub>2</sub>), 3.38 m (8H, CH<sub>2</sub>). <sup>13</sup>C NMR (acetone-D<sub>6</sub>): 13.6 (CH<sub>3</sub>), 20.1 (CH<sub>2</sub>), 24.2 (CH<sub>2</sub>), 59.2 (CH<sub>2</sub>), 151.6 br. [C(NO<sub>2</sub>)<sub>3</sub><sup>-</sup>]. <sup>14</sup>N NMR (acetone-D<sub>6</sub>): 0.0 s (1N, Bu<sub>4</sub>N<sup>+</sup>), 287.6 br.s [3N, C(NO<sub>2</sub>)<sub>3</sub><sup>-</sup>].

### 3.4. Cesium salt of trinitromethane

Tetrabutylammonium salt of trinitromethane (3.9 g, 10 mmol) was dissolved in 60 ml of warm MeOH. A solution of cesium fluoride (2.0 g, 15 mmol in 30 ml of MeOH) was added to the solution of tetrabutylammonium salt of trinitromethane at once. The resulting mixture was stirred for 30 min to complete the precipitation of bright-yellow cesium salt of trinitromethane. The precipitate was collected by filtration and then washed with 1 × 20 ml of cold EtOH and 2 × 20 ml of dichloromethane to yield 2.4 g (85%) of cesium salt of trinitromethane as bright-yellow crystals. Analytical samples were prepared by recrystallization from warm water (30 ml of water per 1 g of salt at 70°C). Due to the instability of this compound at room temperature, the analysis was performed using freshly prepared samples. Anal. calcd for CN<sub>3</sub>O<sub>6</sub>Cs C 4.25, N 14.85, Cs 46.97; found, Cs 47.2. UV–VIS: λ<sub>max</sub> = 350 nm; E = 14,400 (H<sub>2</sub>O). <sup>13</sup>C NMR (DMSO-D<sub>6</sub>): 150.3 br.s [C(NO<sub>2</sub>)<sub>3</sub><sup>-</sup>].

### 3.5. Extraction experiments

Aqueous phases containing 0.023 M of Cs<sup>+</sup>C(NO<sub>2</sub>)<sub>3</sub><sup>-</sup> and 0.023 M of Cs<sup>+</sup>NO<sub>3</sub><sup>-</sup> were used for extraction experiments. Each sample was appropriately traced with Cs-137 at 0.37 μCi/ml. In all experiments, 1 h contacts (1 ml of each phase in 4 ml borosilicate vials) in the dark at 24.5°C were employed by gentle end-over-end rotation at 30 rpm using a Glas-Col rugged rotator. The Cs-137 activity was measured in centrifuge vials using 0.5 ml subsamples by standard γ-counting of the Ba-137m peak at 662 KeV, after allowing at least 1 h for the extracted Cs-137 to reach equilibrium with its Ba-137m daughter. Mass balances were satisfactory (≥97%) in all experiments; no precipitation was observed. Selected results of the experiments are presented in Table 2.

### Acknowledgements

The research was sponsored by the Initiatives for Proliferation Prevention (IPP) program and by the Division of Chemical Sciences, Office of Science, US Department of Energy under contract DE-AC05-96OR22464 with Oak Ridge National Laboratory, managed by Lockheed Martin Energy Research Corporation.

### References

- [1] J. Klein, *Tetrahedron* 39 (1983) 2733.
- [2] A. Rajca, L.M. Tolbert, *J. Am. Chem. Soc.* 110 (1988) 871.
- [3] K.B. Wiberg, *J. Am. Chem. Soc.* 112 (1990) 4177.
- [4] I. Agranat, T.P. Radhakrishnan, W.C. Herndon, A. Skancke, *Chem. Phys. Lett.* 181 (1991) 117.
- [5] A. Gobbi, G. Frenking, *J. Am. Chem. Soc.* 115 (1993) 2362.
- [6] A.M. Krishnan, P. Sjöberg, P. Politzer, J.H. Boyer, *J. Chem. Soc., Perkins Trans. 2* (1989) 1237.
- [7] J. Cioslowski, S.T. Mixon, E.D. Fleischmann, *J. Am. Chem. Soc.* 113 (1991) 4751.
- [8] P. Politzer, P. Lane, *Struct. Chem.* 1 (1990) 159.
- [9] H.M. Niemeyer, *J. Mol. Struct.* 50 (1978) 123.
- [10] K.E. Edgecombe, R.J. Boyd, *Can. J. Chem.* 61 (1983) 45.
- [11] A. Hantzsch, A. Rinckenberger, *Berichte* 32 (1899) 628.
- [12] E. Schmidt, *Berichte* 52 (1919) 400.
- [13] N.V. Grigor'eva, N.V. Margolis, I.N. Shokhor, V.V. Mel'nikov, I.V. Tselinskii, *Zh. Strukt. Khim.* 7 (1966) 278.
- [14] N.I. Golovina, L.O. Atovmyan, *Zh. Strukt. Khim.* 8 (1967) 307.

- [15] N.V. Grigor'eva, N.V. Margolis, I.N. Shokhor, I.V. Tselinskii, V.V. Mel'nikov, *Zh. Strukt. Khim.* 9 (1968) 550.
- [16] B. Dickens, *J. Res. Natl. Bur. Stand. A* 74 (1970) 309.
- [17] K.D. Scherfise, F. Weller, K. Dehnicke, *Z. Naturforsch., Teil B* 40 (1985) 906.
- [18] H.L. Ammon, C.S. Choi, A. Bashir-Hashemi, R.M. Moriarty, J.S. Khosrowshahi, *Acta Crystallogr., Sect. C (Cr. Str. Comm.)* 45 (1989) 319.
- [19] H.L. Ammon, C.S. Choi, R.S. Damavarapu, S. Iyer, J. Alster, *Acta Crystallogr., Sect. C, (Cr. Str. Comm.)* 46 (1990) 295.
- [20] N.V. Podberezskaya, N.V. Pervukhina, V.P. Doronina, *Zh. Strukt. Khim.* 32 (1991) 34.
- [21] H. Bock, T. Hauck, C. Nather, Z. Havlas, *Z. Naturforsch., Teil B* 49 (1994) 1012.
- [22] L. Liang, *Org. Synth.* 21 (1941) 105.
- [23] L.J. Farrugia, *J. Appl. Cryst.* (1997) 565.
- [24] M.N. Burnett, C.K. Johnson, Oak Ridge National Laboratory Report ORNL-6895, 1996.
- [25] J.C. Bryan, M.N. Burnett, A.A. Gakh, *Acta Crystallogr., Sect. C (Cr. Str. Comm.)* 54 (1998) 1229.
- [26] H. Schodel, R. Dienelt, H. Bock, *Acta Crystallogr., Sect. C (Cr. Str. Comm.)* 50 (1994) 1790.
- [27] M.D. Coburn, C.B. Storm, D.W. Moore, T.G. Archibald, *Magn. Res. Chem.* 28 (1990) 16.
- [28] M.Ya. Myagi, E.T. Lippmaa, T.I. Pekhk, S.A. Shevelev, V.I. Erashko, A.A. Fainzilberg, *Izv. Acad. Nauk SSSR, Ser. Khim.* (1967) 730.
- [29] V.I. Erashko, S.A. Shevelev, A.A. Fainzilberg, M.Ya. Myagi, E.T. Lippmaa, *Izv. Acad. Nauk SSSR, Ser. Khim.* (1970) 958.
- [30] E.T. Lippmaa, M.Ya. Myagi, J. Past, S.A. Shevelev, V.I. Erashko, A.A. Fainzilberg, *Izv. Akad. Nauk SSSR, Ser. Khim.* (1971) 1012.
- [31] V.I. Slovetskii, V.I. Erashko, M.K. Orlova, *Izv. Akad. Nauk SSSR, Ser. Khim.* (1970) 1291.
- [32] B.A. Moyer, P.V. Bonnesen, in: A. Bianchi, K. Bowman-James, E. García-España (Eds.), *Physical Factors in Anion Separation Supramolecular, Chemistry of Anions*, Wiley-VCH, New York, 1997, pp. 1–44 Ch. 1; and references therein.
- [33] P.W. Schultz, G.E. Leroi, A.I. Popov, *J. Am. Chem. Soc.* 118 (1996) 10617 and references therein.