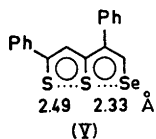


cules per unit cell; density, calc. 1.38, found, 1.39 g/cm³. The experimental error is estimated to be within 0.5 %.

Approximate coordinates for the sulphur and carbon atoms were found from a three-dimensional Patterson synthesis, and the atomic parameters were refined by least squares methods. The coordinates in Table I correspond to the last isotropic refinement cycle. At this stage $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ was 0.17 for 2087 observed reflections. An electron density projection along the *b* axis is reproduced in Fig. 1.

The results show that the sulphur-sulphur distances in (IV) are different, $S_1-S_2 = 2.510 \pm 0.008$ Å and $S_2-S_3 = 2.216 \pm 0.008$ Å. One may therefore conclude that the thiothiophene system in (IV) is perturbed by the presence of phenyl groups in unsymmetrical positions.

A preliminary note on the structure of (V), isosteric with (IV), has recently been published by van den Hendel and Klingsberg.⁸ They find the sulphur-sulphur dis-



tance in (V) to be 2.492 ± 0.003 Å, which is very nearly the same as the equivalent S_1-S_2 distance in (IV). Furthermore, if one subtracts the difference in covalent radii of selenium and sulphur, 0.12 Å, from the selenium-sulphur distance in (V), one arrives at the value 2.21 Å which is close to that found for the S_2-S_3 distance in (IV).

The authors are indebted to Dr. E. Klingsberg, American Cyanamid Co., for providing a sample of (IV).

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Received July 13, 1966.

The Identification of Organic Compounds

VII.* Improved Methods for the Preparation of 3,5-Dinitrobenzoyl Derivatives and Picrates of Aliphatic Amines

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N-Substituted benzamides are often low-melting compounds, and Vecera, Volakova, Kazakova, and Jurecek¹ and Volakova² have therefore proposed to use the *N*-substituted 3,5-dinitrobenzamides for the identification of amines. We are able to recommend these derivatives as they are highly crystalline compounds with melting points distributed over a range of temperature sufficiently wide to differentiate between isomeric compounds.

Unfortunately, the procedure proposed by Vecera *et al.*¹ and Volakova² for the preparation of the derivatives is very troublesome as a standing period of about 12 h is required. We have succeeded in working out a method, described below, by which the preparation of the derivative can be carried out within 10–15 min.

Picrates are also widely used for the characterisation of aliphatic amines. The procedures given in various text-books of organic analysis do not always lead to a precipitation of the picrates although they should be only slightly soluble in the medium used. We have found that the reason is, that the reaction mixture contains an

* Part VI, *Acta Chem. Scand.* **18** (1964) 1353.

excess of the amine. The picrates are very soluble, if more than a slight excess of the amine is present. This is probably due to a complex formation. A modified procedure which avoids this interference is given below.

Experimental. The melting points (corrected) were determined in an electrically heated silicone bath. Rate of heating: 2°/min. The capillary tube was introduced about 15° below the expected melting point. Commercially available amines of analytical grade were used.

Preparation of N-substituted 3,5-dinitrobenz-amides. 3,5-Dinitrobenzoyl chloride (0.4 g, 0.0017 mole) is dissolved in 2 ml of acetone by shaking. 30 ml of ether is added. The amine (ca. 0.004 equiv.) is added *dropwise* to this solution. The mixture is shaken a few seconds after each addition. The amine hydrochloride, which is formed simultaneously with the amide, precipitates, but it does not interfere in the preparation. After the final addition of the amine the solution is shaken with 4 ml 2 N hydrochloric acid in a separatory funnel. The ether layer is isolated and dried with anhydrous calcium chloride. It is then evaporated to dryness.

The crude product which may be an oil, is recrystallized by dissolving it in 5 ml of ethanol by heating. Water is added *dropwise* to the warm solution until a small precipitate occurs. After cooling the derivative is removed by suction in a Büchner funnel and washed on the filter with a few ml of ethanol (50 %). The yield after recrystallisation is about 60–70 %.

Dibenzylamine forms a hydrochloride which cannot be dissolved by addition of 2 N hydrochloric acid. In this case the mixture is filtered after addition of the acid and the ether phase is isolated and evaporated to dryness.

The derivative of benzylamine must be prepared by dissolving 0.4 g of 3,5-dinitrobenzoyl chloride in 10 ml of acetone. The calculated amount of amine is added *dropwise*. The precipitated benzylammonium chloride is dissolved by the addition of 4 ml 2 N hydrochloric acid. After a few minutes of standing *N*-benzyl-3,5-dinitrobenzamide precipitates.

If the amine is present as a salt, about 0.006 equiv. of the salt is shaken vigorously in a separatory funnel with 5 ml of 2 N sodium hydroxide and 20 ml of ether. In order to make the two phases distinguishable two drops of methyl red indicator are added, and the ether phase is isolated and dried by addition of calcium chloride. This phase is used directly in the above procedure.

The following compounds are new: *N*-Benzyl-3,5-dinitrobenzamide, m.p. 201° (Found:

C 55.99; H 3.80; Calc. for $C_{14}H_{11}N_3O_5$: C 55.81; H 3.68). *N*-Phenethyl-3,5-dinitrobenzamide, m.p. 150°. (Found: C 57.28; H 4.31; Calc. for $C_{15}H_{13}N_3O_5$: C 57.14; H 4.16). *DL-N*-(α -Methylbenzyl)-3,5-dinitrobenzamide, m.p. 173°. (Found: C 57.28; H 4.20; Calc. for $C_{15}H_{13}N_3O_5$: C 57.14; H 4.16). *DL-N*-(1-Methylphenethyl)-3,5-dinitrobenzamide, m.p. 147°. (Found: C 58.33; H 4.67; Calc. for $C_{16}H_{15}N_3O_5$: C 58.35; H 4.59). *N,N*-Dibenzyl-3,5-dinitrobenzamide, m.p. 135°. (Found: C 64.38; H 4.50; Calc. for $C_{21}H_{17}N_3O_5$: C 64.44; H 4.38).

A higher melting point than that reported in the literature has been found for four compounds: *N*-Butyl-3,5-dinitrobenzamide, m.p. 105° (lit.¹ 101°); *N-tert*-butyl-3,5-dinitrobenzamide, m.p. 185.5° (lit.¹ 181°); *N*-isopentyl-3,5-dinitrobenzamide, m.p. 139° (lit.¹ 124.5°); *N,N*-diisopropyl-3,5-dinitrobenzamide, m.p. 108° (lit.² 94°).

Preparation of picrates of aliphatic amines. Picric acid (0.2 g, ca. 0.001 mole) is dissolved in 10–15 drops of acetone. 15 ml of ether is added. The amine (ca. 0.001 equiv.) is added *dropwise* to this solution. It is necessary to scratch after each addition. Generally a precipitate is formed after each addition of the amine, but it disappears until nearly equivalent amounts of picric acid and amine are present. It is very important that the amine is not present in excess. The precipitate is removed by filtration on a Büchner funnel and it is washed on the filter with a small amount of ether. The first drop is often pure enough for a melting point determination. It may be recrystallised by dissolving it in a few drops of acetone; it is re-precipitated by addition of 10–15 ml of ether.

A few picrates, e.g. tributylamine picrate and dibutylamine picrate, must be prepared by evaporating the reaction mixture to dryness. The residue is then recrystallised from ethanol or by dissolving it in a small amount of benzene and subsequent addition of ether. The latter procedure is preferred in the case of dibutylamine picrate.

If the amine is present as a salt, about 0.004 equivalents is shaken with 3 ml of 2 N sodium hydroxide and 10 ml of ether. Methyl red indicator is added as described above. After isolation and drying with calcium chloride the ether phase or an aliquot of it is added *dropwise* to a mixture of picric acid (0.2 g), acetone (10–15 drops) and ether (10 ml). Vigorous scratching may be necessary after each addition of amine.

Picrates of about thirty aliphatic amines have been prepared. The melting points were found to be in accordance with those given in the literature. It must be emphasized that

several picrates are polymorphous, and in identifying amines by means of the picrates a careful examination of the literature is necessary before a decision is made.

Di-*sec*-butylamine picrate is a new compound: M.p. 105°. (Found: Equiv.wt. 359.9 (titration with perchloric acid). Calc. for $C_{14}H_{22}N_2O_7$; Equiv.wt. 358.4).

The microanalyses have been performed by Mr. A. Bernhardt, Max Planck-Institut, Mülheim.

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Received September 6, 1966.

The Non-Volatile Acids of Succulent Plants Exhibiting a Marked Diurnal Oscillation in Their Acid Content

III. The Acids of *Kleinia repens* (L.) Haw., *Begonia tuberhybrida* (Hort) and *Mesembryanthemum criniflorum* L. fil.

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The two previous papers in this series^{1,2} deal mainly with the detection of piscidic acid, and its occurrence in *Agave americana* L. and *Opuntia ficus-indica* L. In connection with the following, the authors would also like to draw attention to a third paper dealing with the occurrence of phorbic acid in plants.³

In this paper we submit the results of an investigation of the non-volatile acids of three more species, belonging to three different genera in which typical "crassulacean acid metabolism" has been observed.

For the investigation we used mainly the same methods as in the earlier papers in this series: Isolation of the non-volatile acids over their lead salts, esterification of the acid mixtures, distillation of the ester mixtures in high vacuum, and investigation of the ester fractions by means of gas chromatography, conversion of the acids into hydrazides etc. The gas chromatograph was a Wilkins Autoprep A-700. (Wilkins Instrument and Research, Inc.). The columns used was an aluminium column, 5' 1/4", with Chromosorb 45/60 coated with 2 % SE-30 as solid support, and a copper column, 6' 1/4", with Chromosorb 45/60 coated first with 0.1 % Carbowax 6000 and then with 5 % Apiezon-L as solid support. Helium served as carrier gas. All samples were tested on both columns and co-chromatography of known and unknown samples were carried out.

We also used thin layer chromatography for the detection of minor amounts of phorbic acid. Owing to its dilactone properties, phorbic acid is difficult to handle when subjected to paper or thin layer chromatography. During the investigation we therefore used a method worked out by Anne Kristine Krogh.* This method, which will be published elsewhere, is based on comparative thin layer chromatography of the phorbic acid itself and its lactones under different conditions.

Kleinia repens (L.) Haw. (= *Senecio hawortii*, Sch. Bip.). 3.5 kg of the fresh plant (without roots) gave 40 g of non-volatile acids, of which 35 g were esterified with diazoethane and the ester mixture subjected to fractionation in high vacuum (about 10^{-3} torr). The results of the fractionation and some of the investigations carried out with the different ester fractions and the corresponding acids, are shown in Table 1. The non-identified ester in fractions 1 and 2 gave on the 2 % SE 30 column a peak with a retention time that corresponded to succinic acid diethyl ester, but on the 2 % Apiezon L column the retention time of the peak was different from that of the above-mentioned compound. The non-identified ester made up an almost negligible part of the two fractions.

All the six non-identified esters that were found in fractions 3 and 4 had on both columns shown a longer retention time

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