

09.2-03 STRUCTURAL CHEMISTRY OF TRIARYL

AMINE OXIDATION*. By R. P. Scaringe and S. L. Reynolds, Eastman Kodak Company, Research Laboratories, Rochester, New York.

As part of an experimental study of the structural consequences of triaryl amine oxidation, we have initiated crystallographic investigations of tri(p-tolyl)amine and tri(p-tolyl)aminium hexafluorophosphate. The neutral amine crystallizes in space group $P\bar{1}$, $Z = 4$ and $a = 12.403(1)$, $b = 10.872(1)$, $c = 12.944(2)$, $\alpha = 88.48(1)$, $\beta = 103.34(1)$, $\gamma = 88.93(1)$. The diffraction pattern closely resembles that expected for a crystal belonging to space group $P2_1/c$; the presence of pseudosymmetry did not, however, seriously hinder either the solution of the structure or the refinement process. The structure is in the late stages of refinement and R_F is currently 0.055. The nitrogen atom is very nearly in the plane defined by the three carbon atoms to which it is attached. Agreement between bond parameters of the two independent molecules is generally good. The hexafluorophosphate salt of the radical cation crystallizes in one of the trigonal space groups $P\bar{3}m1$, $P321$ or $P3m1$ with $a = 14.507(2)$ and $c = 8.690(1)$. A complete data set has been collected for this compound and structure analysis is under way.

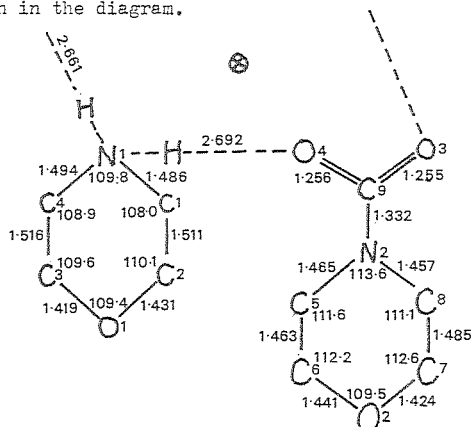
*Acknowledgment: The authors are indebted to Dr. J. H. Perlstein and Ms. E.M.D. Schneider for providing powdered samples of the radical cation salt.

09.2-04 THE CRYSTAL STRUCTURE OF MORPHOLINIUM

MORPHOLINOFORMATE. By C. J. Brown and L. R. Gray, City of London Polytechnic, London E1 7PF, Gt. Britain.

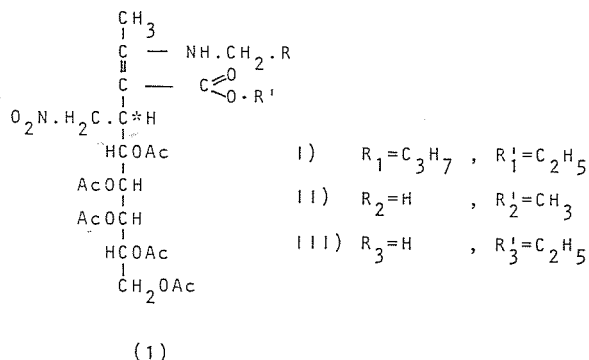
Extraction of the corrosion product formed by metallic lead and white mineral oil at 150° with morpholine gave yellow crystals identical with those produced by bubbling CO_2 gas through morpholine (Knorr, Annalen, (1898), 301, 4). This compound crystallizes in space group $P\bar{1}$ with $a = 10.497$, $b = 9.366$, $c = 6.365$ Å, $\alpha = 94.07$, $\beta = 66.56$, $\gamma = 106.47^\circ$. The structure was determined by MULTAN and refined to $R = 0.06$ for 1473 reflexions.

The structure is evidently a salt $(C_4H_8ONH_2)^+$ $(C_4H_8ONCOO)^-$, and pairs of ions are linked by a closed cyclic hydrogen bonding system. The difference in charge between the anionic and cationic morpholine rings has a notable influence on the bond lengths and angles as shown in the diagram.



09.2-05 CONFORMATIONAL ANALYSES OF α -(1-NITRO-POLYACETOXY-2-HEPTYL)- β -ALKYLAMINO-CROTONIC ACID ESTERS BY X-RAY DIFFRACTION. By R. Vega, M.J. Dianez, A. López Castro and R. Márquez. Departamento de Óptica y Sección de Física del Departamento de Investigaciones Físicas y Químicas del C.S.I.C.. Universidad de Sevilla, Spain.

We report here several examples of α -(1-Nitropolyacetoxy-2-heptyl)- β -alkylamino-crotonic acid esters for which a conformational study is being carried out.



They are by-products in the synthesis of 3-pentaacetoxypentyl-pyrrole derivatives (Gómez-Sánchez, Mancera, Rosado + Bellanato (1980), J.C.S. Perkin Trans, 1, 1199). In the assigned structure (1) a new chiral centre is found (marked with an asterisk) and two diastereoisomers could result; however, only one product was isolated and detected chromatographically. The configuration could not be established from chemical and spectroscopic considerations and an X-ray study was undertaken.

The three compounds belong to the orthorhombic space group $P2_12_12_1$ with four molecules per unit cell.

Crystal data.

I	II	III
$C_{27}H_{42}N_2O_{14}$	$C_{22}H_{32}N_2O_{14}$	$C_{23}H_{34}N_2O_{14}$
$a = 11.147(1)$ Å	$a = 14.270(2)$ Å	$a = 17.367(1)$ Å
$b = 37.350(2)$	$b = 18.743(2)$	$b = 13.176(1)$
$c = 7.705(1)$	$c = 10.309(1)$	$c = 9.446(1)$
$V = 3207.9$ Å ³	$V = 2757.3$ Å ³	$V = 2161.5$ Å ³
$D_c = 1.28$ Mg.m ⁻³	$D_c = 1.31$ Mg.m ⁻³	$D_c = 1.35$ Mg.m ⁻³
$D_o = 1.29$	$D_o = 1.30$	$D_o = 1.36$

Intensity data were collected on an automatic Philips PW 1100 four-circle diffractometer (MoK α for I and CuK α for II and III, graphite monochromator, ω -2 θ scan). The crystal structures have been solved by direct methods and refined by Fourier and least-squares calculations. The main least-squares planes in the molecule and torsion angles have been calculated. The configuration of the sugar chain will be discussed. The molecule in the three compounds has an intramolecular hydrogen bond between the nitrogen and oxygen atoms of the amino and carbonyl groups respectively, showing a chelated structure. The packing is governed by normal van der Waals contacts.