For the preparation of indole at atmospheric pressures from sodium *o*-toluide and carbon monoxide, 14.4 g. (0.6 mole) of sodium hydride was treated with 77 g. (0.72 mole) of *o*-toluidine as described above and carbon monoxide was passed into the reaction flask at 200–210° with stirring until absorption ceased (about thirty minutes). The temperature was then increased to 270–290° for a period of about thirty minutes; yield, 10 g. (0.086 mole) of indole.

The passage of gaseous carbon monoxide into the reaction mixture can be avoided, if instead 0.4 mole of potassium or sodium formate is added prior to the 270–290° heating period. The decomposition of the formate provides the necessary carbon monoxide; yield, 6.0 g. (0.051 mole) of indole with potassium formate and 5.0 g. (0.043 mole) with the use of sodium formate.

Procedure B.—Potassium (46.8 g., 1.2 moles) in liquid ammonia was converted to the amide as previously described and 154 g. (1.44 moles) of *o*-toluidine was added. The liquid ammonia solution was then transferred from the flask by means of glass tubing to the autoclave, which was cooled by a solution of Dry Ice in acetone. After removal of ammonia by gradual heating of the autoclave to 160° and flushing with nitrogen, the autoclave was cooled to room temperature. Carbon monoxide was then added to a pressure of 170 pounds per square inch (0.6 mole). The autoclave was then heated to 300–310° for thirty minutes and upon cooling the reaction mixture was treated for the isolation of indole as previously described; yield, 36 g. (0.31 mole) indole or a yield of 82% based upon *o*-toluidine not recovered.

This process was also carried out in glass apparatus at atmospheric pressure by passage of carbon monoxide into the stirred mixture of potassium *o*-toluidine and excess *o*-toluidine, first at about 190–200° until carbon monoxide ceased to be absorbed (45 minutes) and continuation of carbon monoxide passage at the reaction temperature of 290–310° for ten minutes. The yields based upon unrecovered *o*-toluidine were less than those obtained by holding the carbon monoxide in contact with the reaction mixture within an autoclave.

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Unit Cell and Optical Properties of $t,t,\Delta^{9,11}$-Linoleic Acid[1]

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In a previous paper[2] $t,t,\Delta^{9,11}$-linoleic acid was characterized by X-ray diffraction patterns of powdered specimens. Optical and X-ray diffraction data for single crystals provide a more detailed characterization of this acid, and these data are reported below.

Optical Properties.—Preparation of $t,t,\Delta^{9,11}$-linoleic acid has been described.[2] Single crystals of the acid were obtained by slow evaporation from xylene at 25°. The crystals were monoclinic and occurred as thin, diamond-shaped plates lying on the orthopinacoid, (100), and bounded by the domes, {011}. Inter-edge angles measured in the plane of the plate were 68° and 112°, both ± 1/2°. Since the X-ray data showed that the monoclinic angle was nearly 90°, the inter-edge angles were nearly equal to the interfacial angles of the dome zone. The axial ratio *b*:*c* computed from these angles is 1:1.47, which is in good agreement with the ratio 1:1.48 determined from the X-ray data.

The crystals gave a positive biaxial interference figure; one optic axis was perpendicular to the plate, and the optic axial plane was parallel to the bisector of the acute angle of the plate. The apparent optic axial angle, $2E$, for NaD light was 54° 18′. The optic angle in the crystal was computed to be 34° 46′. The immersion method with NaD light gave 1.527 as the measured value of B.

X-Ray Diffraction Data.—Unit cell dimensions and symmetry elements of $t,t,\Delta^{9,11}$-linoleic acid were determined from diffraction patterns of single crystals taken with a precession camera using copper radiation ($\lambda = 1.539$ kX.). The plane symmetry of zero and n-level patterns placed the crystal in the monoclinic system. Systematic extinction of the general spectra hkl occurred when $h + k$ was odd, and $h0l$ was absent when l was odd, permitting either space group Cc or $C2/c$.

Dimensions of the monoclinic unit cell are $a_0 = 95.69$ kX., $b_0 = 4.95$ kX., $c_0 = 7.31$ kX., and $\beta = 90.6°$. Crystallographic axis a was inclined 0.6° to the plate normal, b bisected the obtuse angle, and c bisected the acute angle of the plate. The observed density of 1.01 is in reasonable agreement with the density, 1.07, computed with the assumption of eight molecules per unit cell.

Crystal Structure.—From the unit cell dimensions and the intensities of the ($h00$) reflections which were observed out to $h = 80$, it is evident that the structure is based on dimeric linoleic acid molecules oriented with their length along the a axis. Since the lattice is C-centered, a_0 (95.69 kX.) corresponds to the projected length of two dimers. The alternation in intensity of the ($h00$) reflections with odd orders strong for $h/2 < 7$ and even orders strong for $7 < h/2 < 20$ is characteristic of the diffraction patterns of all long-chain saturated fatty acids. No reasonable structures based on space group $C2/c$ were found, and it is likely, therefore, that the structure is based on space group Cc with dimers in the general position.

One can estimate the angle of tilt of the linoleic acid dimer with respect to $[d_{001}]$ from the observation that reflection (80.00) is strong. For this reflection to be intense, the contributions of all atoms must be near their maximum values. Considering only the carbon atoms, which must make the major contribution, and assuming the $t,t,\Delta^{9,11}$-linoleic acid dimer to be planar and centrosymmetrical, and to have normal bond angles and lengths, the principal dependence of F_{h00} on α can be expressed by

$$F_{h00} \sim \frac{1}{1 - \cos\,(2\pi ht \cos \alpha)}$$

where α is the angle of tilt measured with respect to $[d_{100}]$ and t is the distance between alternate

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[1] Taken in part from a thesis submitted by L. P. Witnauer in partial fulfillment of the requirements for a Master of Arts degree at Temple University, June, 1948.

[2] L. P. Witnauer, P. L. Nichols, Jr., and F. R. Senti, *J. Am. Oil Chem. Soc.*, **26**, 653 (1949).

carbon atoms (2.52 kX.) expressed as a fraction of d_{100}. For $h = 80$, the denominator of (1) becomes zero at $\alpha = 18.3°$, and F_{h00} attains its maximum value. The direction of maximum polarizability of the crystal, $''\eta_\gamma$, should lie approximately in the direction of the dimers and thus affords another measure of the angle of tilt. η_γ makes an angle of 17° 23′ with $[d_{100}]$, in good agreement with the value of 18.3° derived from the diffraction data. The conventional "angle of tilt," which is the angle of the dimers with respect to the plane of the carboxyl groups, is $90° - \alpha$, or about 72°.

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[3] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture. Article not copyrighted.

NEW COMPOUNDS

Preparation of 2-Bromo-4-nitroethylbenzene and α,α-Dibromo-4-nitroethylbenzene

2-Bromo-4-nitroethylbenzene.—*p*-Nitroethylbenzene,[1] 75.5 g. (0.5 mole) was brominated in the presence of 2.3 g. of iron powder.[2] After the gentle application of heat to start the reaction, a total of 81.6 g. (0.51 mole) of bromine was added at such a rate as to maintain the temperature at 60–70°. After standing over-night the mixture was heated, first on a steam-bath, and finally to 150° until the evolution of hydrogen bromide ceased. The product was washed with dilute sodium bisulfite and water, dissolved in ethyl alcohol, decolorized, dried and concentrated. The residue was distilled under diminished pressure to yield 64 g. (55%), b. p. 155–179° (37 mm.). The distillate partially solidified when cooled to −6°, and the crystalline material was recrystallized repeatedly from ethyl alcohol, and together with some further material from the supernatant liquid, yielded 38.5 g. (34%) of pale yellow prisms, m. p. 31–32°.[3] The material so purified boils at 155–157° (20 mm.).

Anal. Calcd. for $C_8H_8O_2NBr$: C, 41.76; H, 3.50; N, 6.09; Br, 34.73. Found: C, 41.96; H, 3.51; N, 6.2; Br, 34.7.

It was characterized by permanganate oxidation to 2-bromo-4-nitrobenzoic acid, m. p. 170°,[4] which on tin-hydrochloric acid reduction yields *m*-bromoaniline, identified as its acetyl derivative.

α,α-Dibromo-4-nitroethylbenzene.—*p*-Nitroethylbenzene, 83.2 g. (0.55 mole), 2.5 g. of iron powder, 0.2 g. of 20-mesh iron filings, and a crystal of iodine was treated with 175 g. of bromine as above except at 90–100°. After washing the product was steam distilled which removed a much reduced quantity of 2-bromo-4-nitroethylbenzene. The residue, which solidified on cooling, was dissolved in ether, decolorized, dried and the solvent removed, then recrystallized from ethyl alcohol to yield 20.8 g. (12%) of α,α-dibromo-4-nitroethylbenzene as pale yellow needles, m. p. 76–78°.

Anal. Calcd. for $C_8H_7O_2NBr_2$: C, 31.09; H, 2.29; N, 4.53; Br, 51.73. Found: C, 31.35; H, 2.29; N, 4.5; Br, 52.0.

Its identity is tentatively assigned on the bases that permanganate oxidation produces *p*-nitrobenzoic acid which was identified by reduction to *p*-aminobenzoic acid, and while the compound does not produce a precipitate with alcoholic silver nitrate at room temperature, it does on the application of heat.

Attempts to convert 2-bromo-4-nitroethylbenzene into 4-nitro-1,2-diethylbenzene[5] with ethyl bromide and sodium in anhydrous ether were unsuccessful.

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[1] Cline and Reid, THIS JOURNAL, **49**, 3150 (1927).

[2] Ferrum reductum or "iron by hydrogen" was used.

[3] Thermometers calibrated against U. S. P. Melting Point Standards.

[4] Scheufelen, *Ann.*, **231**, 172 (1885).

[5] Lambooy, THIS JOURNAL, **71**, 3756 (1949).

Substituted α-(4-Morpholinyl)-acetonitriles and Related Compounds

The nitriles listed in the table were prepared by one or more of the following methods, adapted from reported procedures: (1) from morpholine and the cyanohydrin in the presence of potassium cyanide,[1] (2) from morpholine, the aldehyde or ketone-sodium bisulfite complex, and potassium cyanide,[1,2] or (3) from morpholine hydrochloride, the carbonyl compound, and potassium cyanide.[3] The recovery and purification of the product was essentially the same for each method: If the product was solid, it was removed by filtration, washed with cold water, and recrystallized from aqueous ethyl alcohol. If the product was an oil, it was extracted with ethyl ether, dried over anhydrous sodium sulfate, and vacuum distilled. Mandelonitrile gave a 55% yield of α-phenyl-α-(4-morpholinyl)-acetonitrile by method 1, whereas 85 and 82% yields, respectively, of the same compound were obtained when benzaldehyde was used in methods 2 and 3. With acetone the yields of nitrile were only 20% by either methods 2 or 3; with formaldehyde the yield was 78% by method 3.

α-Phenyl-α-(4-morpholinyl)-acetamide. A.—A mixture of 3.3 g. of potassium cyanide and 8.1 g. of benzylidene dimorpholine[4] in 20 ml. of water was refluxed on the water-bath until homogeneous (about eleven hours); some ammonia was evolved. The solution was filtered hot after dilution with 20 ml. more of water. Rosettes of needles, m. p. 153.5–154.5,[5] crystallized on cooling; recrystallization from water raised the melting point to 157.5–158.5°. The yield was 4.8 g. or 70%.

Anal. Calcd. for $C_{12}H_{16}O_2N_2$: N, 12.73. Found: N, 12.82.

The compound was readily soluble in alcohol, hot water, and cold concentrated hydrochloric acid, but only slightly soluble in diethyl ether.

B.—Hydrolysis of α-phenyl-α-(4-morpholinyl)-acetonitrile in cold concentrated sulfuric acid gave a product melting at 156° after one recrystallization from water. A mixed melting point with a sample prepared by A was the same. The yield was 4.3 g. or 79% of theory.

α-Phenyl-α-(4-morpholinyl)-thioacetamide.—The crude product as obtained from phenyl morpholinylacetonitrile and hydrogen sulfide by the method of Gabriel and

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[1] Knoevenagel, *Ber.*, **37**, 4082 (1904).

[2] v. Braun, *ibid.*, **41**, 2118 (1908); Bucherer and Schwalbe, *ibid.*, **39**, 2796 (1906).

[3] Strecker, *Ann.*, **75**, 28 (1850); Zelinsky and Stadnikoff, *Ber.*, **39**, 1726 (1906); Marvel and Noyes, THIS JOURNAL, **42**, 2264 (1920).

[4] Zief and Mason, *J. Org. Chem.*, **8**, 5 (1943).

[5] All melting points are corrected.