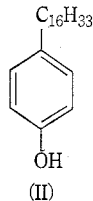
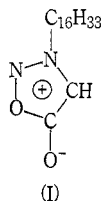


A SURFACE ACTIVE SYDNONE*

By F. H. C. STEWART†

Many members of the group of meso-ionic compounds collectively designated as sydnones have been described in the literature (Baker and Ollis 1957), but no derivatives containing a long-chain alkyl group appear to have been prepared hitherto. In order to investigate the effect of the novel sydnone aromatic nucleus on the properties of a unimolecular film *N*-hexadecylsydnone (I) has now been synthesized.

Ethyl *N*-hexadecylglycinate was prepared from hexadecylamine and ethyl bromoacetate by the general procedure of Speziale and Jaworski (1960). Hydrolysis of the ester gave *N*-hexadecylglycine by way of the sparingly soluble



sodium salt. Nitrosation of *N*-hexadecylglycine was effected in acetic acid solution with excess nitrous fumes. Treatment of the resultant nitroso acid with acetic anhydride gave the required sydnone (I), which was characterized as its C-bromo derivative.

The surface behaviour of the sydnone (I) was examined in a surface trough fitted with a Wilhelmy plate and torsion balance. A stable unimolecular film was formed, and the surface pressure-area curve is reproduced in Figure 1. The original curve was closely followed on repeated expansion and recompression. It is noteworthy that the sydnone (I) spread slowly from powdered crystals

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floating in the surface to an equilibrium pressure of ~ 9 dyne cm^{-1} . Since *N*-hexadecylsydnone (I) may in some respects be considered as a structural analogue of *p*-hexadecylphenol (II) the surface pressure-area curve for the latter (Adam 1923) is also included in Figure 1 for comparison. In both these compounds a hydrophobic paraffin side chain is attached to an aromatic nucleus bearing an oxygen function.

Inspection of molecular models indicates that the *N*-hexadecylsydnone molecule should occupy a minimum area of some 22 \AA^2 in a close-packed monolayer. This is slightly less than the corresponding limiting area of the *p*-hexa-

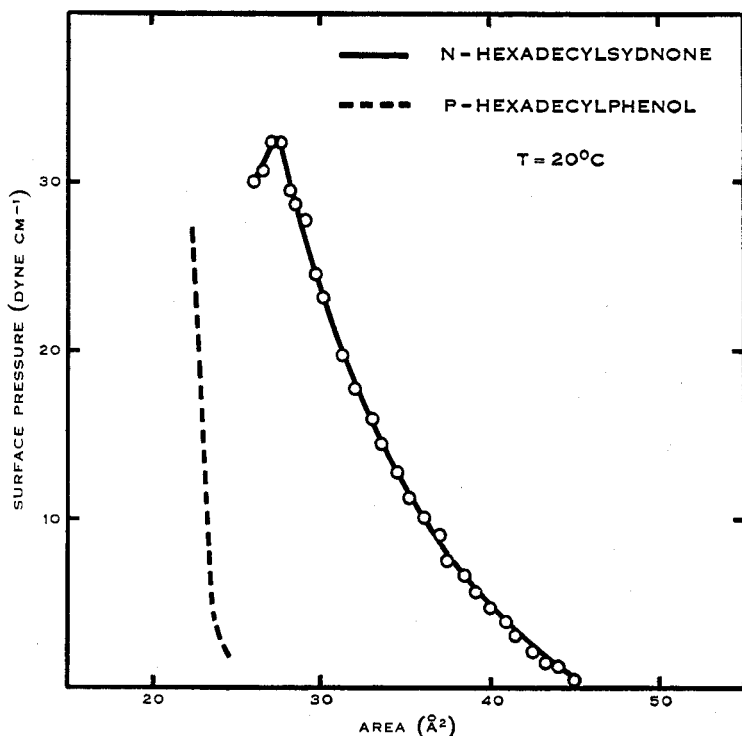


Fig. 1.—Surface pressure-area curves for *N*-hexadecylsydnone and *p*-hexadecylphenol (Adam 1923).

decylphenol monolayer (24 \AA^2 ; Adam 1923). From Figure 1, however, it is seen that whereas the area of the phenol film changes only slightly after the onset of compression at 24 \AA^2 , with the sydnone film compression begins at 46 \AA^2 and proceeds steadily until the monolayer eventually collapses at $\sim 28 \text{ \AA}^2$.

The expanded nature of the sydnone monolayer and its collapse before attainment of the geometrical minimum area suggests that the lateral cohesion of the film is appreciably less than in the condensed phenol monolayer. This may be due to electrostatic repulsion between the highly polar sydnone nuclei, and would agree with the accepted meso-ionic formulation of these compounds (as I).

Experimental

The microanalyses were carried out by the Australian Microanalytical Service, C.S.I.R.O. and University of Melbourne. All melting points are uncorrected. The surface measurements were carried out at room temperature, and the film was spread from a solution of the sydnone (1 mg/ml) in a benzene-light petroleum mixture (1:1).

(a) *Ethyl N-Hexadecylglycinate*.—A solution of commercial hexadecylamine (72 g) and triethylamine (30 g) in benzene (200 ml) was treated with ethyl bromoacetate (47.5 g) in benzene (100 ml) over 2–3 hr, and the mixture stirred overnight at room temperature. The triethylamine hydrobromide which separated was filtered off, and the solvent removed *in vacuo*. Distillation of the residue gave a crude product (28.5 g), b.p. 194–212 °C/2 mm, which was redistilled to give the pure ester, b.p. 194–204 °C/2 mm. Yield 14.8 g (15%) (Found: N, 4.8%. Calc. for $C_{20}H_{41}NO_2$: N, 4.3%). The ester was a colourless oil which solidified at 0 °C, and then apparently underwent a slow phase transformation from a translucent to an opaque form.

The hydrochloride formed colourless needles from light petroleum containing a little ethanol, m.p. 178–179 °C (Found: C, 66.0; H, 11.7; N, 3.7%. Calc. for $C_{20}H_{42}ClNO_2$: C, 66.0; H, 11.7; N, 3.8%).

(b) *N-Hexadecylglycine*.—The foregoing ester (2.0 g) was dissolved in ethanol (20 ml), and a solution of NaOH (1.0 g) in a little water added. The mixture was refluxed for 30 min, and cooled. The sparingly soluble sodium salt of *N*-hexadecylglycine was filtered off, washed with ethanol, and dried. It formed colourless crystals, m.p. 255–257 °C (decomp.) (Found: N, 4.5%. Calc. for $C_{18}H_{36}NO_2Na$: N, 4.4%).

The sodium salt was dissolved in glacial acetic acid with gentle warming, and the solution diluted with water to precipitate the free amino acid, which was recrystallized from ethanol to give needles, m.p. 174–176 °C. Yield 1.35 g (74%) (Found: C, 72.5; H, 12.3; N, 4.9%. Calc. for $C_{18}H_{37}NO_2$: C, 72.2; H, 12.5; N, 4.7%).

(c) *N-Nitroso-N-hexadecylglycine*.—A solution of *N*-hexadecylglycine (0.6 g) in glacial acetic acid (40 ml) was briefly cooled in ice-water, and then saturated with nitrous fumes. After keeping at 0–5 °C for several hours water was added, and the precipitated nitroso compound collected and dried. Recrystallization from light petroleum gave colourless needles, m.p. 89–90 °C. Yield 0.65 g (98%) (Found: C, 65.9; H, 11.2; N, 8.6%. Calc. for $C_{18}H_{36}N_2O_3$: C, 65.9; H, 11.1; N, 8.5%). The compound gave a positive Liebermann reaction. Other methods of nitrosation were unsuccessful.

(d) *N-Hexadecylsydnone (I)*.—A mixture of the nitroso acid (0.5 g) and acetic anhydride (10 ml) was kept for 3–4 days at room temperature in the dark, with gentle warming at intervals to maintain complete solution. The excess anhydride was decomposed with water, and the precipitated sydnone filtered off, washed, and recrystallized from aqueous ethanol. The compound formed colourless needles, m.p. 63.5–64.5 °C. Yield 0.33 g (70%) (Found: C, 69.8; H, 11.0; N, 9.3%. Calc. for $C_{18}H_{34}N_2O_2$: C, 69.6; H, 11.1; N, 9.0%). The infrared spectrum had a strong carbonyl band at 1735 cm^{-1} .

Bromination in acetic anhydride at 0 °C gave the *C*-bromo derivative, which formed almost colourless needles from ethanol, m.p. 66.5–67.5 °C (Found: N, 7.3%. Calc. for $C_{18}H_{33}BrN_2O_2$: N, 7.2%).

References

- ADAM, N. K. (1923).—*Proc. Roy. Soc. A* **103**: 676.
BAKER, W., and OLLIS, W. D. (1957).—*Quart. Rev.* **11**: 15.
SPEZIALE, A. J., and JAWORSKI, E. G. (1960).—*J. Org. Chem.* **25**: 728.